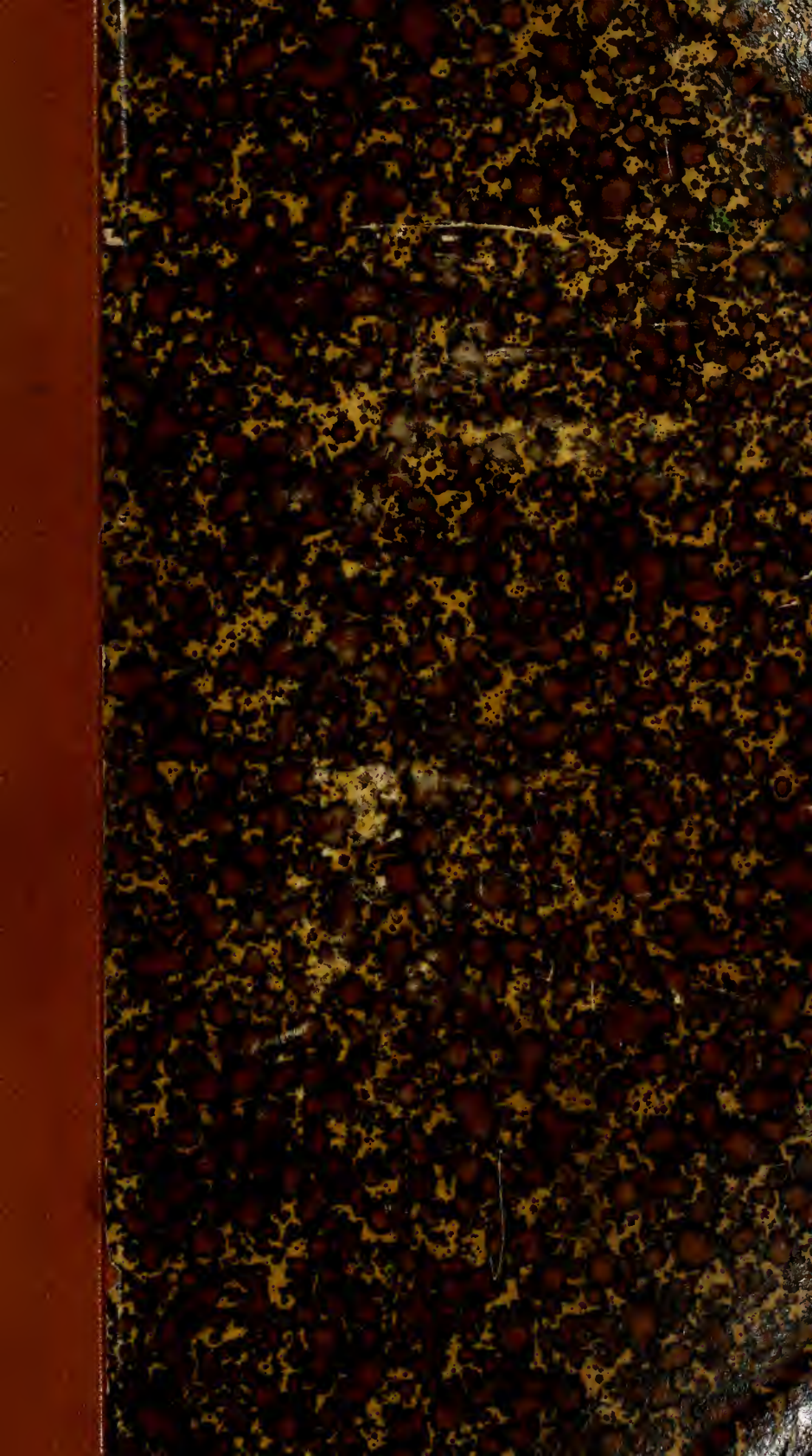




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AMERICAN CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of Harvard College.

ON THE CONDENSATION OF NITROMALONIC ALDEHYDE WITH BENZYL METHYL KETONE.¹

BY HENRY B. HILL AND WILLIAM J. HALE.

The condensation of various ketones with nitromalonic aldehyde has been the subject of much investigation in this laboratory. From the simpler reaction with acetone,² resulting in the ready formation of paranitrophenol, to the more involved cases with ketone acids,³ the same mode of formation has been clearly made out, and no more confirmatory evidence regarding the nature of these condensations need be supplied. The formation of an intermediate product, a derivative of dihydrobenzol, seems established, which, by the addition and elimination of a molecule of water, passes into the phenol proper. The action of benzylmethyl ketone, in accordance with results just cited, must give a derivative of phenylbenzol, a 5-nitro-2-

¹ This paper was written after the untimely death of Professor Hill.—W. J. H.

² This JOURNAL, 22, 89 (1899).

³ *Ibid.*, 24, 1 (1900).

oxydiphenyl, and constitutes, therefore, an interesting field for the investigation of a number of hitherto unknown diphenyl derivatives.

Although this work was begun several years ago and a preliminary notice had appeared in the Spring of 1900,¹ an earlier article by Borsche² on the action of diazobenzol chloride upon an alkaline solution of nitrosophenol was found to overlap a portion of our work. As Borsche had not chosen to continue the study of the nitrodiphenyls it seemed advisable for us to turn our attention to the investigation of these compounds and to determine the relative positions of the nitro groups by comparison with the parent substance—the direct product of this synthesis.

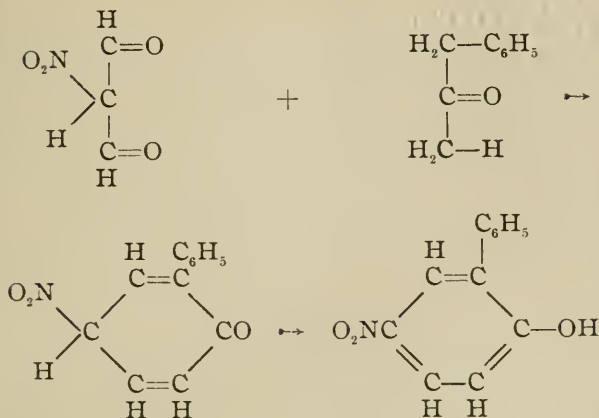
The compound obtained by Borsche was a nitrosooxydiphenyl. From it he prepared the amido body, the quinone and hydroquinone, and by the action of nitric acid a dinitro derivative. These bodies have been obtained in the course of our investigations, but the melting-points are, in most instances, several degrees higher than those given by Borsche. In a second paper by Borsche³ the conversion of the nitrosooxydiphenyl into the nitrooxydiphenyl by the action of very dilute nitric acid is described. This compound is the starting-point in our work, and results directly from the condensation of nitromalonic aldehyde with benzylmethylketone. The constitution of these compounds, as first determined by Borsche, appeared somewhat doubtful, but in the light of further investigations published in his second paper, and more particularly by these syntheses from nitromalonic aldehyde, the entire matter of constitution is definitely established.

When benzylmethyl ketone reacts with sodium nitromalonic aldehyde, in slightly alkaline solution, there is formed the sodium salt of 1-phenyl-4-nitrophenol, *i. e.*, 5-nitro-2-oxydiphenyl. The first stage in this condensation must be considered as the formation of 1-nitro-3-phenyl-4-keto-2,5-dihydrobenzol, which passes over at once into the phenol :

¹ Ber. d. chem. Ges., **33**, 1241 (1900).

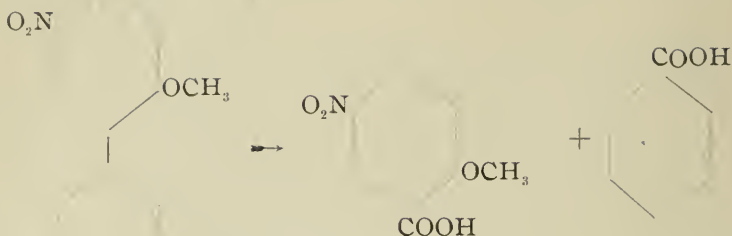
² *Ibid.*, **32**, 2935 (1899).

³ Ann. Chem. (Liebig), **312**, 211 (1900).

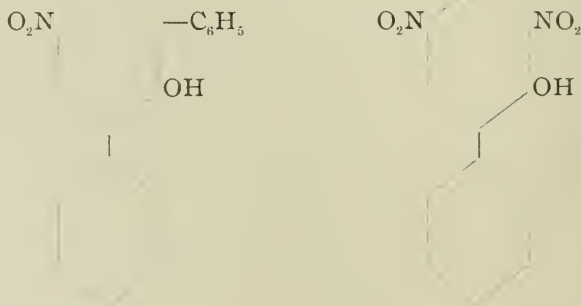


The phenol is readily liberated from the deep red solution of its sodium salt by means of a current of carbon dioxide. The sodium salt crystallizes in beautiful orange-red prisms, which change to crimson upon dehydration. The action of alkyl haloids upon this sodium salt, as well as that of benzoyl chloride upon the oxydiphenyl itself, gives mono derivatives which show conclusively but one hydroxyl present. From the nitro-oxydiphenyl was prepared the amido compound, and then the quinone, but owing to the appearance of Borsche's paper, further research in this line was discontinued and our attention given entirely to a study of the nitrooxydiphenyl itself.

When nitric acid acts upon 5-nitro-2-oxydiphenyl, in glacial acetic acid solution, another nitro group enters the substituted ring, and there is formed the 5,3-dinitro-2-oxydiphenyl. The nitro group naturally enters meta to the nitro group and ortho to the hydroxyl already present. The sodium salt of this dinitro compound crystallizes better than the sodium salt of the mononitro derivative, and appears in beautiful orange-red leaflets, containing 2 molecules of water of crystallization. The structure of the mononitrooxydiphenyl is readily established by the oxidation of its methyl ether with chromic acid mixture. The resulting products are 5-nitrosalicylic acid methyl ether, and benzoic acid,



In attempting to establish the constitution of the dinitro-oxydiphenyl by the oxidation of its ethers little or no oxidation-product could be obtained. In order, however, to substantiate the theory of its constitution an indirect method was adopted. The 2,6-diphenyl-4-nitrophenol of Soch and Oen-slager¹ may be regarded as the 5-nitro-2-oxydiphenyl in which the 3-position is occupied by a phenyl group :

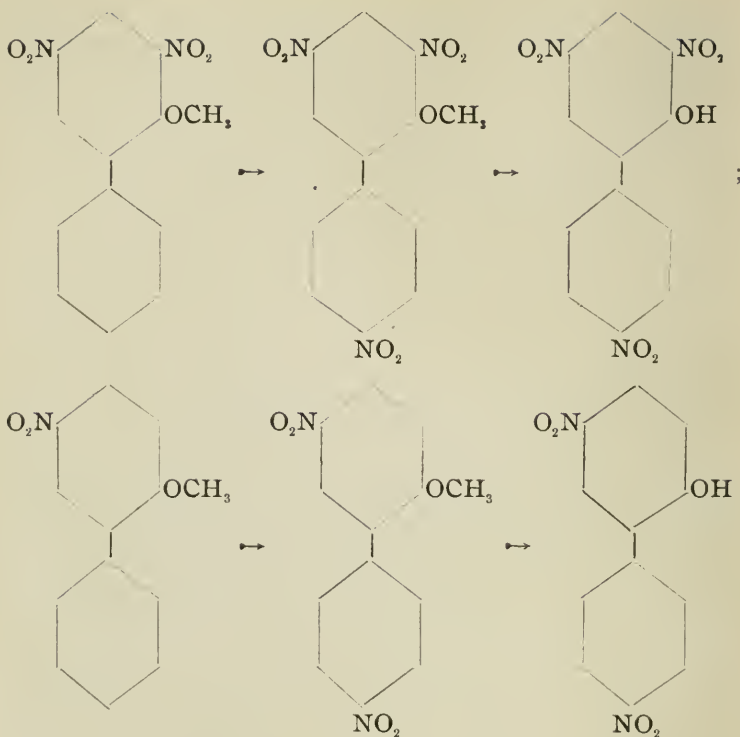


This body, on treatment with nitric acid in glacial acetic acid, does not give a dinitro compound such, for example, as was so easily obtained from 5-nitro-2-oxydiphenyl. As the 3-position—the only free position meta to the 5-nitro group—is the natural place for a second nitro group to enter, and as this position is already filled in the 5-nitro-2-oxy-1,3-diphenyl-

¹ This JOURNAL, **24**, 5 (1900).

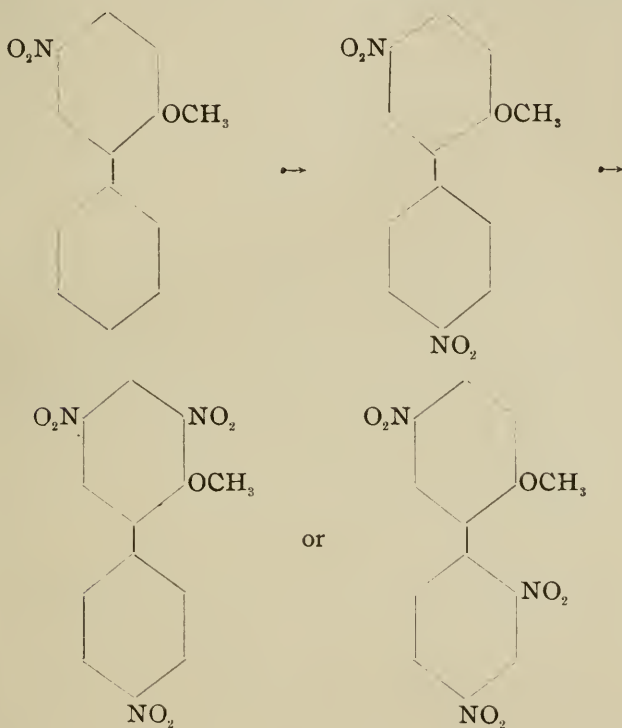
benzol of Soch and Oenslager, we have reason to believe that at this 3-position the second nitro group enters the 5-nitro-2-oxydiphenyl, forming thus a 5,3-dinitro-2-oxydiphenyl. When the mono- or dinitrooxydiphenyls are subjected to treatment with boiling nitric acid, the phenyl group bearing the hydroxyl is completely oxidized. Benzoic acid, however, or what might be expected in the presence of strong nitric acid—metanitrobenzoic acid—does not result, but in its place paranitrobenzoic acid is obtained. This is proof conclusive that the nitro group must have entered the free phenyl ring para to the tie existing before the oxidation took place. In order to establish the identity of this paranitrobenzoic acid the silver salt and methyl ester were made and analyzed.

The action of nitric acid upon the ethers was found to give additional nitro compounds and these, in turn, by saponification, could be converted into their corresponding nitrooxydiphenyls. The methyl ether of 5,3-dinitro-2-oxydiphenyl, on treatment with boiling nitric acid, passes into a 5,3,4'-trinitro-2-oxydiphenyl methyl ether. The free trinitrooxydiphenyl, obtained by the saponification of this ether, gave, on treatment with boiling nitric acid, paranitrobenzoic acid, which shows that the third nitro group must have entered the second ring para to the tie. When the 5-nitro-2-oxydiphenyl methyl ether is dissolved in glacial acetic acid and then treated with nitric acid, only one additional nitro group enters. This nitro group enters the second ring para to the tie, thus producing 5,4'-dinitro-2-oxydiphenyl methyl ether, which, in turn, may be converted into the free 5,4'-dinitro-2-oxydiphenyl by saponification with hydrochloric acid. 5,4'-Dinitro-2-oxydiphenyl is isomeric with 5-3-dinitro-2-oxydiphenyl and, by treatment with nitric acid in acetic acid solution, can be converted into 5,3,4'-trinitro-2-oxydiphenyl, the same compound as is obtained from the ether of 5,3-dinitro-2-oxydiphenyl. This is proof sufficient to show that in 5,4'-dinitro-2-oxydiphenyl the nitro group has entered the second ring para to the tie :



If the 5-nitro-2-oxydiphenyl methyl ether is treated with boiling nitric acid, the 5,4'-dinitro-2-oxydiphenyl methyl ether at first formed is converted, by further nitration, into a trinitro-2-oxydiphenyl methyl ether. This third nitro group can enter the first phenyl ring meta to the nitro group already present, and give 5,3,4'-trinitro-2-oxydiphenyl methyl ether; or it can enter the second phenyl ring meta to the nitro group that has previously entered, and thus produce a 5,2',4'-trinitro-2-oxydiphenyl methyl ether. As a matter of fact, both of these isomers are obtained in about equal quantity and can be readily separated by means of their respective solubilities in alcohol. The one, 5,3,4'-trinitro-2-oxydiphenyl methyl ether has already been mentioned; the other, 5,2',4'-trinitro-2-oxydiphenyl methyl ether, was saponified with hydrochloric acid

and the free trinitro-2-oxydiphenyl subjected to oxidation by the action of boiling nitric acid. The benzoic acid formed proved to be metadinitrobenzoic acid, thus showing the relation of the two nitro groups in the second phenyl ring :



EXPERIMENTAL PART.

*Benzylmethyl Ketone.*¹—Twenty to thirty grams phenyl acetic acid are boiled with a large excess of calcium carbonate in a liter of water. The hot, filtered solution is then evaporated to dryness upon a steam-bath, and the residue of calcium phenyl acetate dried at 120° to 130° for several hours. At this temperature the salt melts, and when cooled presents a vitreous appearance. The finely pulverized calcium phenyl acetate, deprived of its moisture, is now mixed with a large

¹ Ber. d. chem. Ges., 3, 198 (1870).

excess of pulverized calcium acetate, also dried at 120° . This mixture, placed in a non-tubulated retort, yields, on distillation, dibenzyl ketone, benzyl methyl ketone, and acetone. The dark-red, oily distillate thus obtained is freed of its acetone by warming upon a water-bath, and then shaken up, at ordinary temperatures, with four to five times its volume of a saturated aqueous solution of sodium acid sulphite. As ketones possessing methyl groups unite much more readily with acid sodium sulphite than do those without these groups, the crystalline product that separates on standing will consist entirely of the benzylmethyl ketone acid sulphite salt. Upon filtering off these crystals the dibenzyl ketone still adhering may be completely removed by washing with ether. The acid sodium sulphite salt of benzylmethyl ketone, by treatment with a strong solution of sodium carbonate, is readily resolved into neutral sodium sulphite and the free ketone, the latter rising to the surface as a colorless oily liquid which, after removal, should again be warmed on the water-bath to drive off any traces of acetone. Thirty grams calcium phenyl acetate, with 45 grams calcium acetate, gave 7.2 grams purified benzylmethyl ketone.

5-Nitro-2-oxydiphenyl, $C_6H_5 \cdot C_6H_3(NO_2)(OH)$.—A solution of sodium nitromalonic aldehyde¹ in six times its weight of water, to which has been added 1 molecule of sodium hydroxide in normal solution, is allowed to react with the equivalent amount of benzylmethyl ketone, dissolved in four to five times its weight of alcohol. The alcohol prevents the precipitation of the ketone by aqueous sodium hydroxide and thus enables the reaction to run to completion. The time necessary for this condensation is about twelve hours. A further addition of sodium hydroxide does not materially increase the yield of product nor shorten the time, while, with the alkali in amount less than 1 molecule, the time for complete reaction is considerably lengthened. The mixture does not require shaking, but reacts well by standing at ordinary temperatures. When reaction is complete the excess of alcohol is evaporated over the water-bath and the deep red liquid, cooled and some-

¹ This JOURNAL, 22, 89 (1899).

what diluted by the addition of water, is saturated with carbon dioxide. The 5-nitro-2-oxydiphenyl soon separates as a yellow crystalline precipitate which, after removal to a filter, is well washed with cold water. In this manner 88.2 per cent of the theoretical yield was obtained. The use of hydrochloric acid for acidification proved undesirable, owing to the viscous form in which the phenol was precipitated.

5-Nitro-2-oxydiphenyl crystallizes best from dilute acetic acid in long, yellow needles, which melt at 125° to 126° (corr.), (126° to 128° Borsche).

It is readily soluble in acetone or in alcohol, and may be crystallized from dilute alcohol. It is fairly soluble in ether, chloroform, benzol, or carbon disulphide, but insoluble in ligroin. Boiling water dissolves it sparingly, 10,000 parts water dissolving 17.2 parts phenol, and from this aqueous solution the phenol again separates on cooling. 5-Nitro-2-oxydiphenyl sublimes beautifully in yellow needles.

I. 0.1791 gram substance gave 0.4408 gram CO_2 and 0.0732 gram H_2O .

II. 0.1462 gram substance gave 8.3 cc. moist N at 20° and 778 mm. pressure.

	Calculated for $\text{C}_{12}\text{H}_9\text{O}_3\text{N}$.	I.	Found.	II.
C	66.94	67.14		
H	4.22	4.57		
N	6.55			6.62

The Sodium Salt of 5-Nitro-2-Oxydiphenyl.—The sodium salt is readily soluble in alcohol or water, and may be crystallized from its concentrated aqueous solution in the form of orange-red prisms which contain 3.5 molecules of water of crystallization. Nearly all of this crystal water is slowly lost over sulphuric acid, but to remove the last traces the salt must be dried at 120° to 125° . At the same time the orange-red color is changed into the crimson of the anhydrous salt.

I. 0.6676 gram salt lost, at 125° , 0.1398 gram H_2O .

II. 0.4858 gram salt lost, at 125° , 0.1020 gram H_2O .

III. 0.2324 gram air-dried salt gave 0.0551 gram Na_2SO_4 .

	Calculated for $C_{12}H_8O_3NNa.3\frac{1}{2}H_2O$.	I.	Found. II.	III.
H_2O	21.01	20.94	21.00	
Na	7.68			7.69

5-Nitro-2-oxydiphenyl Methyl Ether,

$C_6H_5.C_6H_3(NO_2)(OCH_3)$.—The methyl ether is easily prepared by the action of methyl iodide upon the sodium salt. After three to four hours boiling upon the water-bath, under a reflux condenser, the clear solution is evaporated to dryness and extracted with ether. From the ethereal solution large clusters of needles separate on evaporation. The methyl ether is most readily soluble in hot alcohol, from which, on cooling, it crystallizes in beautiful colorless needles. It is insoluble in water, but readily soluble in ether, chloroform, acetone, benzol, or carbon disulphide, and fairly soluble in hot ligroin, from which also it may be crystallized. The melting-point is $95^{\circ}.2$ (corr.).

0.1585 gram substance gave 0.3972 gram CO_2 and 0.0726 gram H_2O .

	Calculated for $C_{13}H_{11}O_3N$.	Found.
C	68.09	68.36
H	4.84	5.12

5-Nitro-2-oxydiphenyl Ethyl Ether,

$C_6H_5.C_6H_3(NO_2)(OC_2H_5)$.—This was prepared in the same manner as the methyl ether by the action of ethyl iodide upon the sodium salt. It is similar in its solubilities and in other respects to the methyl ether. After several crystallizations from alcohol the melting-point became constant at $110^{\circ}.6$ (corr.).

0.1414 gram substance gave 0.3576 gram CO_2 and 0.0702 gram H_2O .

	Calculated for $C_{14}H_{13}O_3N$.	Found.
C	69.10	68.98
H	5.39	5.55

5-Nitro-2-oxydiphenyl Benzoic Ether,

$C_6H_5.C_6H_3(NO_2)(OCOC_6H_5)$.—When the 5-nitro-2-oxydi-

phenyl, made into a paste with a small amount of water, is shaken up with benzoyl chloride, and sufficient sodium hydroxide solution added to give an alkaline reaction, a precipitate is formed which, on crystallization from hot alcohol, appears in small, white, irregular prisms, melting at $99^{\circ}.3$ (corr.). This product is readily soluble in chloroform, carbon disulphide or hot alcohol, but insoluble in water. It is fairly soluble in benzol, ether, acetone, glacial acetic acid, or hot ligroin.

0.1772 gram substance gave 0.4628 gram CO_2 and 0.0692 gram H_2O .

	Calculated for $\text{C}_{19}\text{H}_{13}\text{O}_4\text{N}$.	Found.
C	71.45	71.24
H	4.11	4.37

5-Amido-2-oxydiphenyl, $\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_3(\text{NH}_2)(\text{OH})$.—The 5-nitro-2-oxydiphenyl was reduced to the amido compound by tin and hydrochloric acid in alcoholic solution; gentle warming greatly facilitates the reduction. After the tin has been removed by the action of hydrogen sulphide, and the mother-liquor sufficiently concentrated, crystals of the hydrochlorate appear. This gives, by treatment with a solution of potassium carbonate, a white precipitate of the free base which, owing to impurities present, rapidly darkens on exposure to the air. 5-Amido-2-oxydiphenyl is fairly soluble in carbon disulphide or in hot benzol, crystallizing from the latter as the solution cools. It is sparingly soluble in ether or chloroform, insoluble in ligroin or water, but soluble in hot alcohol, from which it crystallizes well in small, colorless needles, melting at 198° to 199° (corr.) (192° Borsche).

0.1388 gram substance gave 0.3945 gram CO_2 and 0.0798 gram H_2O .

	Calculated for $\text{C}_{12}\text{H}_{11}\text{ON}$.	Found.
C	77.79	77.52
H	5.98	6.43

2-Phenylbenzoquinone, $\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_3\text{O}_2$.—The 5-amido-2-oxydiphenyl, dissolved in forty times its weight of dilute sulphuric

acid (1 part acid to 3 parts water), was treated with sodium dichromate, in excess of the requisite amount, dissolved in four times its weight of water. Gentle warming upon the water-bath was found necessary to start the reaction. The mixture was then allowed to stand several hours, after which the quinone was removed by extraction with ether. 2-Phenylbenzoquinone is readily soluble in ether, chloroform, or carbon disulphide, and fairly soluble in ligroin, benzol, acetone, or hot water, crystallizing from water on cooling. It dissolves readily in warm alcohol, and crystallizes from it slowly, but is best crystallized out of dilute acetic acid (80 per cent), from which it separates in orange-yellow leaflets, melting at 112° to 113° (corr.) (107° to 108° Borsche).

0.1112 gram substance gave 0.3184 gram CO_2 and 0.0488 gram H_2O .

	Calculated for $\text{C}_{12}\text{H}_8\text{O}_2$.	Found.
C	78.24	78.11
H	4.38	4.91

5,3-Dinitro-2-oxydiphenyl, $\text{C}_6\text{H}_5 \cdot \text{C}_6\text{H}_2 \cdot (\text{NO}_2)_2 \cdot (\text{OH})$. — The 5-nitro-2-oxydiphenyl was dissolved in twelve to fifteen times its weight of glacial acetic acid by gently warming, and four to five times its weight of nitric acid (sp. gr. 1.40) then added. From this warm solution there separates, almost immediately, yellow crystals of the dinitrooxydiphenyl. The product is obtained in a very pure condition, and in an amount equal to 95 per cent of the theoretical. This dinitrooxydiphenyl sublimes in the form of yellow needles like the mononitrooxydiphenyl, but with less ease. It is sparingly soluble in ether or carbon disulphide, insoluble in ligroin, and very sparingly soluble in hot water. It dissolves in benzol, chloroform, acetone, alcohol, ethyl acetate, or glacial acetic acid when hot, and from each crystallizes on cooling. The crystals obtained from acetone or ethyl acetate are in the form of small elongated octahedra, while from alcohol, benzol, or glacial acetic acid they appear in long, saw-teeth aggregations. From glacial acetic acid, its best solvent, the purified product melts at 207° to 208° (corr.) (203° to 204° Borsche).

I. 0.2144 gram substance gave 0.4338 gram CO_2 and 0.0654 gram H_2O .

II. 0.2286 gram substance gave 22.1 cc. moist N at 23° and 775 mm. pressure.

	Calculated for $\text{C}_{12}\text{H}_8\text{O}_5\text{N}_2$.	I.	Found.	II.
C	55.36	55.17		
H	3.10	3.41		
N	10.80			11.06

The Sodium Salt of 5,3-Dinitro-2-oxydiphenyl.—By dissolving the dinitrooxydiphenyl in a hot solution of sodium hydroxide it is at once converted into the sodium salt which separates as the solution cools. The sodium salt, though fairly soluble in hot water, is only sparingly soluble in cold. It crystallizes beautifully from its aqueous solution in glistening, orange-red leaflets, which lose their water of crystallization slowly over sulphuric acid, more rapidly at 100° to 105° , and change color to the crimson of the anhydrous salt. A solution of the sodium salt may be decomposed by carbon dioxide and the dinitrooxydiphenyl thus liberated.

I. 0.4924 gram air-dried salt lost, at 100° to 105° , 0.0554 gram H_2O .

II. 0.2408 gram air-dried salt lost, at 100° to 105° in two hours, 0.0272 gram H_2O .

III. 0.2438 gram air-dried salt gave 0.0542 gram Na_2SO_4 .

	Calculated for $\text{C}_{12}\text{H}_7\text{O}_5\text{N}_2\text{Na} \cdot 2\text{H}_2\text{O}$.	I.	Found.	III.
			II.	
H_2O	11.32	11.25	11.30	
Na	7.24			7.21

5,3-Dinitro-2-oxydiphenyl Methyl Ether,

$\text{C}_6\text{H}_5 \cdot \text{C}_6\text{H}_2 \cdot (\text{NO}_2)_2 \cdot (\text{OCH}_3)$.—By the action of methyl iodide upon the sodium salt of dinitrooxydiphenyl, the methyl ether is formed, but the reaction runs too slowly for practical purposes. The silver salt, prepared by the action of silver nitrate upon a solution of the sodium salt, was found to work much better, and accordingly was treated with methyl iodide and methyl alcohol, under a reflux-condenser, upon a water-bath. After boiling for several hours, the clear alcoholic solution was

poured off and evaporated; small yellow crystals of the methyl ether soon separate, which, after repeated crystallization from alcohol, are obtained in colorless leaflets, melting at 114° to 115° (corr.). This methyl ether is fairly soluble in ether or in hot ligroin, and from the latter it may be crystallized. It is insoluble in water, but quite readily soluble in benzol or glacial acetic acid, crystallizing fairly well from 40 per cent acetic acid.

0.2356 gram substance gave 0.4902 gram CO_2 and 0.0832 gram H_2O .

	Calculated for $\text{C}_{13}\text{H}_{10}\text{O}_5\text{N}_2$.	Found.
C	56.90	56.75
H	3.67	3.95

5,3-Diamido-2-oxydiphenyl, $\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_2\cdot(\text{NH}_2)_2\cdot(\text{OH})$.—The reduction of the dinitrooxydiphenyl by tin and hydrochloric acid was carried on in alcoholic solution in the same manner as described in the reduction of the mononitrooxydiphenyl. The colorless crystals of the hydrochlorate thus obtained, upon treatment with potassium carbonate, gave a yellow flocculent precipitate, which changed rapidly to a reddish-brown powder when dry. The diamidooxydiphenyl is soluble in alcohol or in glacial acetic acid, insoluble in ether, ligroin, or chloroform. The alcoholic solution, on dilution with water, gave a brown-red precipitate, but no definitely crystalline substance with a melting-point could be obtained.

Oxidation of the 5-Nitro-2-oxydiphenyl Methyl Ether.—In attempting to oxidize the free phenyl group in this compound, by the use of potassium permanganate in neutral or in alkaline solution, no successful results were obtained. In all cases the methyl ether remained unacted upon and could be completely recovered. The use of chromic acid in acetic acid solution, as carried out by Hammarsten,¹ proved much more satisfactory than the usual method of potassium dichromate with sulphuric acid. Under such conditions the methyl ether was readily resolved into the acids possible from the two phenyl rings. Mononitrooxydiphenyl methyl ether was boiled vigor-

¹ Ber. d. chem. Ges., 14, 71 (1881).

ously, under a reflux condenser, with forty times its weight of 20 per cent solution of chromium trioxide dissolved in glacial acetic acid. After a half hour's boiling the cooled solution was poured into a small quantity of water and the aqueous mixture extracted with ether. The residue from the ether extract was then treated with a solution of sodium carbonate to dissolve the acid oxidation-products, and, at the same time, to leave undissolved the unchanged methyl ether. In this case the absence of methyl ether indicated that the oxidation was complete. The clear solution of the sodium salts, after acidification with hydrochloric acid, was again extracted with ether, and afforded a white product melting at 125° to 140° . This product was now distilled with steam; all of it dissolved readily in the hot water and a portion which distilled over with the aqueous vapor after extraction from the distillate by ether, proved to be benzoic acid, melting sharply at 120° . The contents of the flask, on extraction with ether, gave a white solid melting at 147° to 149° , evidently the 5-nitrosalicylic acid methyl ether melting at 148° to 149° .¹

Oxidation of the 5,3-Dinitro-2-oxydiphenyl Methyl Ether.—This proved to be a much more difficult task. Even with the strongest chromic acid mixtures no appreciable quantity of acid oxidation products was taken up by the sodium carbonate solution as previously employed. In all cases the residue was the unchanged methyl ether. Although 5,3-dinitrosalicylic acid methyl ether may have been produced in this manner, the quantity was insufficient for its complete identification.

Nitric Acid and the Nitrooxydiphenyls.—The dinitrooxydiphenyl undergoes vigorous oxidation when boiled for fifteen to twenty minutes, with twenty times its weight of nitric acid (sp. gr. 1.40), in a long-necked flask, the neck serving as a reflux condenser. A large amount of carbon dioxide is evolved, and on cooling small white crystals of paranitrobenzoic acid separate from the reaction-mixture. In like manner the mononitrooxydiphenyl, heated with twenty times its weight of strong nitric acid, gives the same result, but as this compound does not dissolve readily in the nitric acid, the time

¹ Ann. Chem. (Liebig), **150**, 6 (1869); **173**, 41 (1874).

necessary for the oxidation is about twice that required for the dinitrooxydiphenyl. The crystalline product in each case melted at 226° to 234° . It crystallizes from water in leaflets and melts at 233° to 234° , whereas paranitrobenzoic acid melts at 238° .

0.2178 gram substance gave 0.3982 gram CO_2 and 0.0612 gram H_2O .

	Calculated for $\text{C}_7\text{H}_5\text{O}_4\text{N}$.	Found.
C	50.27	49.84
H	3.02	3.14

The silver salt of this oxidation product was made by first forming the ammonium salt and then precipitating the aqueous solution with silver nitrate. It was purified by crystallization from hot water, from which it separated in white needle clusters.

0.1775 gram silver salt, dried over sulphuric acid, gave 0.1222 gram AgBr.

	Calculated for $\text{C}_7\text{H}_4\text{O}_4\text{NAg}$.	Found.
Ag	39.38	39.55

As a further means of identification the methyl ester of this oxidation product was made. Not only from the silver salt by treatment with methyl iodide, but also from the free acid itself by the action of hydrochlorated methyl alcohol; the product obtained was the methyl ester of paranitrobenzoic acid. This ester is readily soluble in ether, benzol, alcohol, or hot ligroin, and after crystallization from ligroin or dilute alcohol appears in glistening leaflets, which melt at 94° to 95° . The melting-point given by Beilstein is 96° . The identity of the products obtained by these two methods shows conclusively that there is no phenolic hydroxyl present, and therefore leads to the conclusion that the phenyl ring bearing the hydroxyl in the original nitrooxydiphenyl is completely broken up. The production of paranitrobenzoic acid would naturally point to the presence of some ortho- or metanitrobenzoic acid in the oxidation mixture, but no meta-acid whatever was found, and

only the smallest traces of orthonitrobenzoic acid could be isolated from the mother-liquors.

Action of Nitric Acid upon the Nitrooxydiphenyl Methyl Ethers.

5,3,4'-Trinitro-2-oxydiphenyl Methyl Ether, $C_6H_4(NO_2).C_6H_2(NO_2)_2.(OCH_3)$. — The 5,3-dinitro-2-oxydiphenyl methyl ether was boiled under a reflux condenser for twenty minutes with twenty times its weight of nitric acid (sp. gr. 1.40). From the reaction mixture, transferred to an open vessel and concentrated over the water-bath to one-third its volume, small, elongated prisms separate on cooling, which melt at 165° to 167° , but on further crystallization from glacial acetic acid melt at 170° to 171° (corr.). The yield is almost quantitative. This trinitrooxydiphenyl methyl ether is readily soluble in chloroform, ethyl acetate, or boiling glacial acetic acid, fairly soluble in benzol, and only sparingly soluble in ether or boiling alcohol. It is insoluble in ligroin or water.

0.1352 gram substance gave 0.2420 gram CO_2 and 0.0386 gram H_2O .

	Calculated for $C_{13}H_9O_7N_3$.	Found.
C	48.88	48.82
H	2.84	3.19

5,3,4'-Trinitro-2-oxydiphenyl, $C_6H_4(NO_2).C_6H_2(NO_2)_2.(OH)$. — When the trinitrooxydiphenyl methyl ether, melting at 170° to 171° , is heated with a large excess of concentrated hydrochloric acid, in a sealed tube, at 180° to 190° , for from six to seven hours, saponification takes place and there is formed the free trinitrooxydiphenyl and methyl chloride. The contents of the tube, were diluted with water, filtered, and the yellow product collected. This trinitrooxydiphenyl was dissolved by warming in a solution of sodium hydroxide; the clear red liquid thus obtained showed that the saponification was complete; after acidification with hydrochloric acid, the yellow precipitate of trinitrooxydiphenyl was crystallized from hot alcohol; it melts at 163° to 164° (corr.), and consists of pointed, light yellow prisms, irregular in form. It is readily soluble in benzol, ether, or chloroform, fairly soluble in glacial acetic acid or

carbon disulphide, and insoluble in ligroin or water. It may also be crystallized from dilute acetic acid. The sodium salt of this compound is soluble in alcohol, and though readily soluble in hot water, is only fairly so in cold, crystallizing from water in matted globular aggregations of an orange-red color.

0.1818 gram substance gave 0.3138 gram CO_2 and 0.0454 gram H_2O .

	Calculated for $\text{C}_{12}\text{H}_7\text{O}_7\text{N}_3$.	Found.
C	47.18	47.08
H	2.31	2.79

5,3,4'-Trinitro-2-oxydiphenyl, on treatment with twenty times its weight of boiling nitric acid (sp. gr. 1.40), for some twenty minutes, gave crystals of paranitrobenzoic acid, melting at 235° to 238° .

5,4'-Dinitro-2-oxydiphenyl Methyl Ether, $\text{C}_6\text{H}_4(\text{NO}_2).\text{C}_6\text{H}_3(\text{NO}_2).(\text{OCH}_3)$.—A solution of 5-nitro-2-oxydiphenyl methyl ether, in ten times its weight of glacial acetic acid, was treated with three to four times its weight of nitric acid (sp. gr. 1.40), and after gentle boiling for some ten to twelve minutes under a reflux condenser, was allowed to cool. A white crystalline mass of needle-clusters readily separated. The same product may be obtained when the 5-nitro-2-oxydiphenyl methyl ether is dissolved in concentrated nitric acid, but the solution must be immediately diluted with water and rapidly cooled, in order to prevent further nitration. 5,4'-Dinitro-2-oxydiphenyl methyl ether is soluble in one hundred parts of hot alcohol, from which it crystallizes in very fine white needles. It is soluble in warm glacial acetic acid, or in hot benzol, crystallizing from each as the solution cools. It is also readily soluble in chloroform, sparingly in ether, and insoluble in ligroin or water. After repeated crystallization from alcohol the melting-point became constant at 222° to 223° (corr.).

0.1560 gram substance gave 0.3247 gram CO_2 and 0.0546 gram H_2O .

	Calculated for $\text{C}_{13}\text{H}_{10}\text{O}_5\text{N}_2$.	Found.
C	56.90	56.80
H	3.67	3.91

5,4'-Dinitro-2-oxydiphenyl, $C_6H_4(NO_2).C_6H_3(NO_2).(OH)$.—The 5,4'-dinitro-2-oxydiphenyl methyl ether is converted into the free oxydiphenyl by heating for from five to six hours with concentrated hydrochloric acid, in a sealed tube, at 200 to 210°. The product, filtered from the diluted acid mixture, was dissolved by warming with a solution of sodium hydroxide. This clear red liquid, filtered from traces of unsaponified methyl ether, was then acidified with hydrochloric acid to reprecipitate the nitrooxydiphenyl. 5,4'-Dinitro-2-oxydiphenyl crystallizes best from dilute alcohol (50 per cent.) in long slender needles, of a pale yellow color, melting at 224° to 225° (corr.). It is readily soluble in alcohol, ether, chloroform, or glacial acetic acid, moderately soluble in hot benzol, and insoluble in ligroin or water.

0.1284 gram substance gave 0.2596 gram CO_2 and 0.0380 gram H_2O .

	Calculated for $C_{12}H_8O_5N_2$.	Found.
C	55.35	55.14
H	3.10	3.31

The sodium salt is fairly soluble in cold water, and readily so in hot, crystallizing out in small orange-red needle clusters. When 5,4'-dinitro-2-oxydiphenyl is boiled with twenty times its weight of nitric acid (sp. gr. 1.40) paranitrobenzoic acid results, as in the oxidation of the nitrooxydiphenyls previously described. If, however, the compound is dissolved in glacial acetic acid, and a small quantity of nitric acid added, there separates, upon dilution with water, a yellow precipitate of the 5,3,4'-trinitro-2-oxydiphenyl melting at 163° to 164°, the same product as is obtained from the 5,3-dinitro-2-oxydiphenyl.

5,2',4'-Trinitro-2-oxydiphenyl Methyl Ether, $C_6H_3(NO_2)_2.C_6H_3(NO_2)(OCH_3)$.—When 5-nitro-2-oxydiphenyl methyl ether is boiled under a reflux condenser, for twenty-five to thirty minutes, with twenty times its weight of nitric acid (sp. gr. 1.40), and the solution, after evaporation to one-third its volume over the water-bath, is allowed to stand, there separates a white crystalline product, melting at 105° to 120°. These crystals, dried and finely powdered, were extracted with

a considerable quantity of warm alcohol. The residue, after several crystallizations from glacial acetic acid, melted at 170° to 171° (corr.), and is therefore the 5,3,4'-trinitro-2-oxydiphenyl methyl ether. The clear alcoholic solution, on evaporation, gave a white crystalline product, which, after several crystallizations from alcohol, appeared in small flattened prisms, melting at 104° to 106° (corr.). The two compounds thus isolated are produced in equal quantities, and in almost quantitative yields. The same results are obtained when the 5,4'-dinitro-2-oxydiphenyl methyl ether is treated with boiling nitric acid; therefore the compounds are seen to be isomeric. 5,2',4'-Trinitro-2-oxydiphenyl methyl ether is readily soluble in chloroform, ether, benzol, ethyl acetate, glacial acetic acid, or hot alcohol, but almost insoluble in ligroin. It may be crystallized from benzol and ligroin, and also from dilute acetic acid.

0.1392 gram substance gave 0.2483 gram CO_2 and 0.0392 gram H_2O .

	Calculated for $\text{C}_{13}\text{H}_9\text{O}_7\text{N}_3$.	Found.
C	48.88	48.66
H	2.84	3.15

5,2',4'-Trinitro-2-oxydiphenyl, $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2)(\text{OH})$.—This compound results upon the saponification of 5,2',4'-trinitro-2-oxydiphenyl methyl ether with concentrated hydrochloric acid. The reaction is conducted in a sealed tube, at a temperature of 160° to 170° , for five or six hours. The crude product was dissolved in a solution of sodium hydroxide, and the clear red solution of the sodium salt acidified with hydrochloric acid, the nitrooxydiphenyl separating as a pale yellow precipitate. It is readily soluble in chloroform, fairly so in glacial acetic acid, warm alcohol, or warm benzol, sparingly in ether, and insoluble in ligroin. It crystallizes from dilute acetic acid, but better from benzol and ligroin, in small pointed yellow prisms, melting at 152° to 153° (corr.). The sodium salt is fairly soluble in cold water, readily so in hot, and crystallizes in small orange-red needle-clusters.

0.1030 gram substance gave 0.1780 gram CO_2 and 0.0254 gram H_2O .

	Calculated for $\text{C}_{12}\text{H}_7\text{O}_7\text{N}_3$.	Found.
C	47.18	47.14
H	2.31	2.66

When this 5,2',4'-trinitro-2-oxydiphenyl is boiled with twenty times its weight of nitric acid (sp. gr. 1.40), for twenty to thirty minutes, and the reaction mixture cooled, white crystals of 2,4-dinitrobenzoic acid separate. After crystallization from dilute acetic acid the melting-point rose to that of the pure acid, 179° . This indicates that the two nitro groups in the second phenyl ring are meta to one another.

THE REACTION BETWEEN ORGANIC MAGNESIUM COMPOUNDS AND UNSATURATED COMPOUNDS.

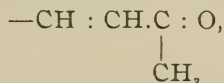
II. REACTIONS WITH DERIVATIVES OF CINNAMIC ACID.

BY E. P. KOHLER AND GERTRUDE HERITAGE.

The experiments described below were made in continuation of a study of the properties of substances containing the conjugated system,



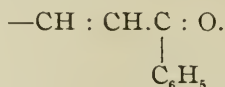
In the first paper¹ it was shown that the reaction between substances of this type and organic magnesium compounds varies in a remarkable way with the atoms or groups in combination with the carbon atom of the carbonyl group. The reaction is always one of direct addition, but in the case of aldehydes and of those ketones that contain the group



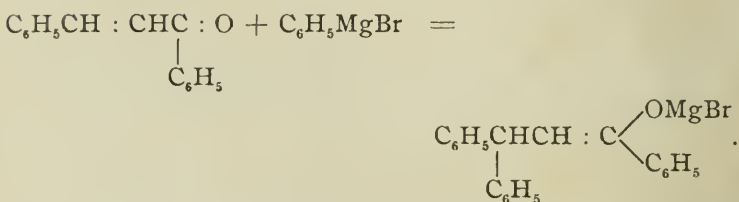
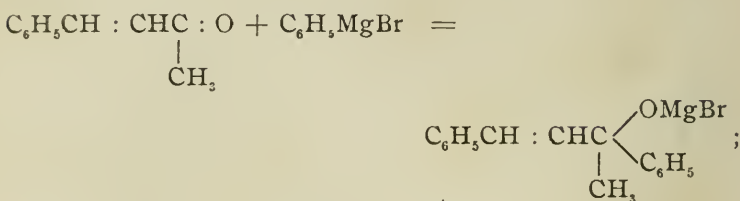
the magnesium compound combines exclusively with the car-

¹ This JOURNAL, 31, 642.

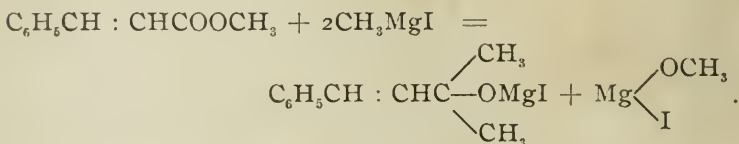
bonyl group, while only 1,4-addition takes place when the ketone contains the group



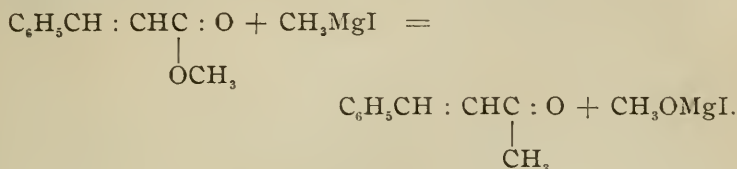
Two typical reactions are illustrated by the following equations :



In the first paper only aldehydes and ketones—substances that have either hydrogen or a hydrocarbon residue in combination with the carbonyl group—were considered. In this paper the list is materially increased; the results show the influence of alkoxy groups in esters, of chlorine in an acid chloride, and of a secondary amine residue in a substituted acid amide. It will be seen that the principal reaction with all of these substances consists in 1,4-addition of the magnesium compound to the conjugated system. The reactions of methylmagnesium iodide apparently form an exception, as these invariably give magnesium derivatives of an unsaturated tertiary alcohol :

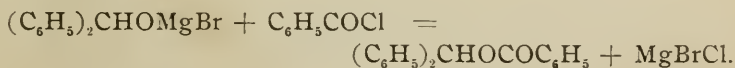


The reason for this is evident. The magnesium compound which, as is known, reacts considerably more readily than the corresponding aromatic compounds, first replaces the methoxyl group with methyl :



The result is an unsaturated ketone of the type that gives only 1,2-addition-products with magnesium compounds. This explanation is supported by the fact that, when the ordinary method of procedure is reversed, so that the magnesium compound is gradually added to an excess of the ester, it is possible to isolate a considerable quantity of the unsaturated ketone.

The method of proving that 1,4-addition had taken place in any given case, was the same as that used in the work described in the previous paper ; the magnesium compound was treated with benzoyl chloride, and the formation of an ester of benzoic acid was regarded as proof that the magnesium had been in combination with oxygen. In support of this method, it has been found that when magnesium compounds, in which the magnesium is undoubtedly linked to oxygen, are treated with benzoyl chloride under the same conditions, they readily react to form esters of benzoic acid. When benzaldehyde, for example, reacts with phenylmagnesium bromide, the product must have the magnesium linked to oxygen because it gives benzhydrol when decomposed with water. When the magnesium compound before decomposition with water, is treated with benzoyl chloride, it gives a very good yield of benzhydrol benzoate :

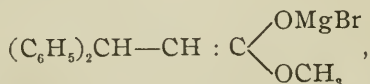


The magnesium compounds described below are, so far as

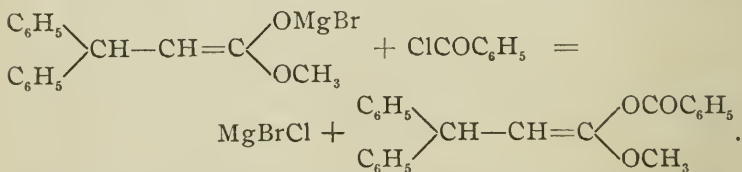
we know, the only 1,4-addition-products of α,β -unsaturated acids that have thus far been obtained. Their formation and properties lend strong support to Thiele's view that the "apparent activity" of the double union between the carbon atoms of this type of unsaturated acids is due to the possibility of 1,4-addition to the conjugated system,



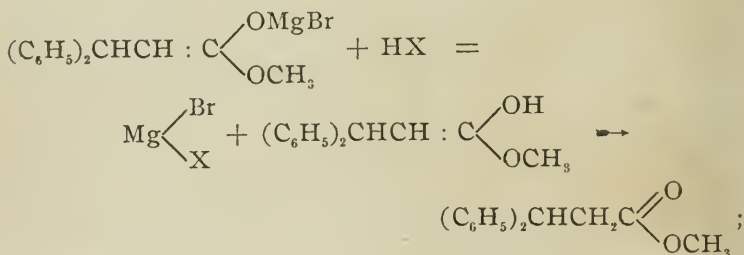
In most cases the product formed by 1,4-addition to this group immediately undergoes rearrangement, but, by reason of its peculiar composition, a magnesium compound, like that represented by the formula

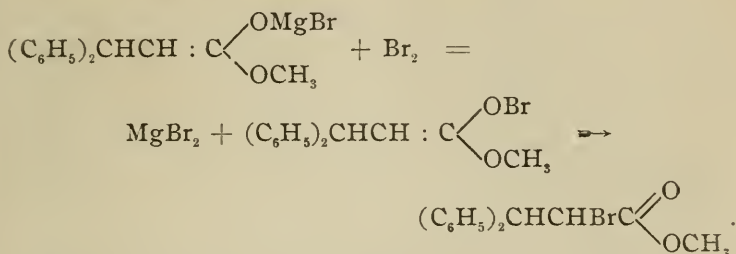


is stable. The corresponding acyl derivatives are also capable of existence, hence there is no rearrangement when the magnesium compound reacts with an acid chloride :



The corresponding hydrogen and halogen compounds, on the other hand, represent types that are, as is known, extremely unstable, hence the products formed by the action of water, of acids and of the halogens, on these magnesium compounds, immediately undergo rearrangement into a more stable form :





Before describing the experiments we desire to point out that this paper deals only with the primary products obtained by the reaction under consideration. The addition-products, obtained by 1,4-addition of magnesium compounds to unsaturated compounds, as a rule, readily combine with more of the unsaturated compound and, unless special precautions are taken, the final result is a mixture of a number of exceedingly complex substances. With methyl cinnamate and phenylmagnesium bromide, for example, we have obtained no less than five of these complex secondary products that we expect to consider in a subsequent paper.

EXPERIMENTAL.

I. Reactions with Esters.

Methyl Cinnamate and Phenylmagnesium Bromide: Methyl β, β -Diphenylpropionate, $(\text{C}_6\text{H}_5)_2\text{CHCH}_2\text{COOCH}_3$.—A dilute ethereal solution of the ester was added, drop by drop, to a solution of the magnesium compound that was kept at -10° in a freezing-mixture. Each drop of the ester produced a yellow precipitate that redissolved until the liquid contained somewhat more than 1 molecule of ester for 2 molecules of the magnesium compound. At this stage the yellow compound no longer disappeared even after vigorous shaking, hence the addition of ester was discontinued. The liquid was allowed to remain in the freezing-mixture for two hours, and for one more hour at the ordinary temperature. It was then poured into a separating funnel containing finely crushed ice and shaken until the magnesium compound was completely decomposed. After dissolving the magnesium salts in iced hydrochloric acid, the

ethereal layer was separated washed, and dried with sodium sulphate. The ethereal solution, on evaporation in a current of dry air, left an oil that partially solidified in a freezing-mixture. The solid was removed as completely as possible by adding low-boiling ligroin to the oil and filtering. After one recrystallization from alcohol it was found to be pure diphenylpropionophenone. The ligroin was evaporated and the oily residue exposed to a low winter temperature for several days, when it solidified almost completely. The solid was dried on a porous plate, and recrystallized from a mixture of ligroin and ether. An analysis gave the following results :

0.1640 gram substance gave 0.4798 gram CO_2 and 0.1004 gram H_2O .

	Calculated for $\text{C}_{16}\text{H}_{16}\text{O}_2$.	Found.
C	80.00	79.73
H	6.66	6.79

The substance has the composition of a methyl ester of diphenylpropionic acid. It gave β,β -diphenylpropionic acid when hydrolyzed, and it was further identified by comparison with a specimen of the ester obtained by boiling β,β -diphenylpropionic acid with a 3 per cent. solution of hydrochloric acid in methyl alcohol. The ester crystallizes from ether or ligroin in large lustrous prisms that melt at 47° . It is readily soluble in alcohol, ether, and boiling ligroin; moderately soluble in cold ligroin.

These results show that the phenyl group in the magnesium compound goes to one end of the conjugated system, but they do not indicate the fate of the magnesium atom. To locate this the magnesium compound was prepared as before, and treated with an ethereal solution of benzoyl chloride, containing 1 molecule of the chloride for each atom of magnesium used in the preparation of phenylmagnesium bromide. The reaction took place in the cold, the product separating as a crystalline solid. This was filtered off, washed with dilute hydrochloric acid and recrystallized from acetone. It was thus separated into two benzoyl compounds, one of which—the less

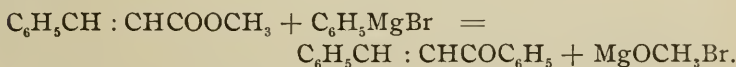
soluble—was the benzoic acid ester described in a previous paper. The more soluble substance is much less stable. After repeated solution in cold acetone and precipitation with absolute alcohol it was obtained in long, silky, white needles, melting at 130° to 133°. An analysis gave the following results :

0.1591 gram substance gave 0.4668 gram CO₂ and 0.0861 gram H₂O.

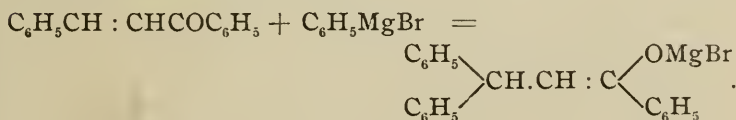
	Calculated for C ₂₃ H ₂₀ O ₃ .	Found.
C	80.23	80.00
H	5.83	6.01

The compound is evidently a benzoate, since it is very easily hydrolyzed to benzoic acid and methyl diphenylpropionate. For this purpose it is sufficient to suspend the substance in water and distil in a current of steam ; benzoic acid passes into the distillate while pure diphenylpropionic ester remains behind. These results may be summed up as follows :

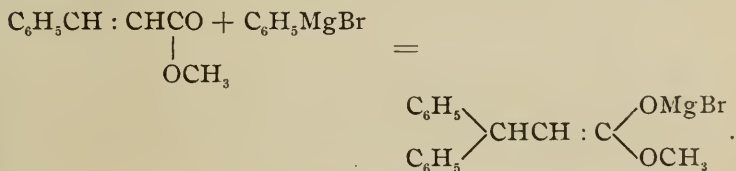
1. Some of the ester reacts with phenylmagnesium bromide like an ester of a saturated acid, giving the corresponding ketone :



This ketone immediately combines with a second molecule of the magnesium compound :



2. The rest of the ester combines directly with the magnesium compound :



The relative amounts of ketone and ester formed vary with the temperature. At -10° the amount of ketone obtained rarely exceeds 5 per cent. of the entire product, while at the temperature of boiling ether, the amount may rise to 20 per cent.

The relative amounts of ketone and ester produced also vary with the different esters of cinnamic acid. The ethyl ester gives only a trace of ketone at -10° , and less than 10 per cent at the temperature of boiling ether. The amyl ester gives only a trace of ketone at the higher, and none at the lower temperature.

Methyl Cinnamate and Methylmagnesium Iodide: Dimethyl-

styryl *see errata p. 647*
~~*styryl*~~ Carbinol: $\text{C}_6\text{H}_5\text{CH} : \text{CHC} \begin{array}{l} \nearrow \text{CH}_3 \\ \searrow \text{CH}_3 \end{array} \text{—OH}$.—The substances were

allowed to react under a variety of different conditions. In some experiments an ethereal solution of the ester was gradually added to an excess of the magnesium compound at the temperature of a freezing-mixture; in others the reaction was carried out in boiling ether and in still others in boiling benzene. The result was the same in all cases. After removing the magnesium salts and evaporating the ether, there remained an oil from which no solid substances could be obtained and which could not be distilled, even in a vacuum, without decomposition. As the oil was not hydrolyzed when boiled with alcoholic potash, it contained no ester, and because it gave no oxime when boiled with an alcoholic solution of hydroxylamine hydrochloride and potassium hydroxide, it contained no ketone. It readily reduced cold alkaline solution of potassium permanganate.

Twenty grams of the oil, suspended in ice-water, were treated with a cooled solution of potassium permanganate until no further reduction took place. Nearly all of the oil went into solution; the rest was extracted with ether. The oxides of manganese were filtered off and the filtrate concentrated on a water-bath. On acidifying the concentrated solution benzoic acid was precipitated. This was filtered off and a small quan-

tity of the same acid that remained in solution removed by distillation in a current of steam. From the liquid left after distillation ether extracted a different acid, which remained as a crystalline solid when the ether was evaporated. This was found to be oxyisobutyric acid. It melted at 79° and sublimed at the temperature of the water-bath. These oxidation-products—benzoic and oxyisobutyric acids—show that the reaction between methyl cinnamate and methylmagnesium iodide, results mainly in the formation of the tertiary alcohol,

$\text{C}_6\text{H}_5\text{CH} : \text{CHC} \begin{array}{l} \nearrow \text{CH}_3 \\ \text{—OH} \\ \searrow \text{CH}_3 \end{array}$, the oxidation taking place at the double linkage.

The part of the product that was not affected by the oxidizing agent was less than 5 per cent of the whole. It was a volatile oil, with a very pronounced, characteristic odor and was not formed by the permanganate because the same oil was obtained by distilling the original product in a current of steam. It boils under diminished pressure without decomposition, most of it distilling at 128° under a pressure of 11 mm. The fraction boiling at this temperature gave the following results on analysis :

0.1611 gram substance gave 0.5086 gram CO_2 and 0.1264 gram H_2O .

	Calculated for $\text{C}_{22}\text{H}_{26}\text{O}$.	Found.
C	86.28	86.10
H	8.50	8.72

The composition of the substance corresponds to that of an ether represented by the formula $[\text{C}_6\text{H}_5\text{CH} : \text{C}(\text{CH}_3)_2]_2\text{O}$. The substance combines with bromine and reduces boiling alkaline solution of potassium permanganate. Since it is evidently a very subordinate product of the reaction, it was not investigated any further.

When an ethereal solution of methylmagnesium iodide is slowly siphoned into a solution of the ester that is kept in a freezing-mixture, the product contains a considerable quantity

of benzalacetone, in addition to the substances described above. This was isolated as follows: The oil was first distilled with steam to remove the ether, then dried in an evaporating dish on the water-bath and repeatedly extracted with low-boiling ligroin. The ligroin solution, on evaporation, left an oil that partially solidified when seeded with a crystal of benzalacetone. The solid was dried on a porous plate and recrystallized from ligroin. It melted sharply at 36° , the melting-point of benzalacetone, and gave dibenzalacetone with benzaldehyde and sodium hydroxide. The yield was small 4.8 grams of ketone from 20 grams of methyl cinnamate.

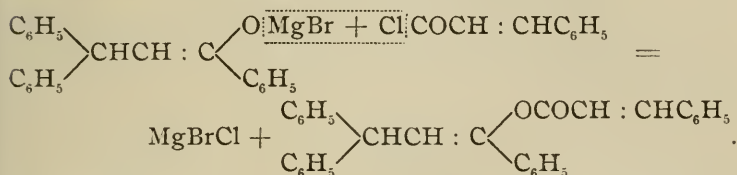
II. Reactions with Cinnamyl Chloride.

Cinnamyl Chloride and Phenylmagnesium Bromide.—The substances reacted energetically when brought together in dilute ethereal solution at -20° . The product, separated in the usual way, was a thick viscous liquid that evidently contained a number of different substances. After removing some bromobenzene and diphenyl by distillation in a current of steam and a small quantity of cinnamic acid by extraction with boiling water, the remainder of the product was boiled for two hours with alcoholic potash, and the solution evaporated to dryness. A partial separation of the residue was obtained by boiling with water and filtering. The part that was insoluble in water—approximately 20 per cent of the entire product—was recrystallized from alcohol. It was mainly diphenylpropionophenone mixed with complex substances that were not investigated.

From the aqueous solution, which contained potassium chloride and potassium salts of organic acids, dilute hydrochloric acid precipitated two acids that were separated by fractional recrystallization from boiling water. One was cinnamic acid, the other β,β -diphenylpropionic acid.

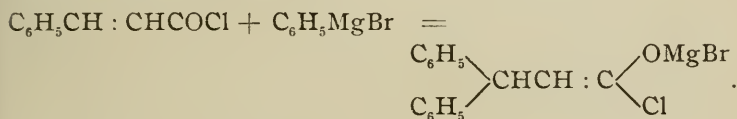
It is evident, from these results, that the primary reactions of cinnamylchloride are exactly like those of the esters of cinnamic acid. A part of the chloride reacts like chlorides of

saturated acids and forms an unsaturated ketone—benzalacetophenone. This combines with a second molecule of phenylmagnesium bromide to form a magnesium compound that, in turn, reacts with a second molecule of the chloride :



When the resulting cinnamate is boiled with alcoholic potash it gives potassium cinnamate, and diphenylpropiofenone.

Another part of the acid chloride combines directly with phenylmagnesium bromide.



The resulting magnesium compound also reacts with an additional molecule of the acid chloride. The product is a cinnamate that, when decomposed with alcoholic potash, gives potassium cinnamate, and the potassium salt of diphenylpropionic acid.

III. Reactions with the Ethyl Anilide of Cinnamic Acid.

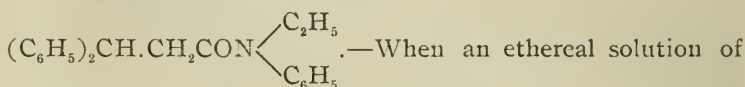
Cinnamyl Ethyl Anilide, $\text{C}_6\text{H}_5\text{CH} : \text{CHCON}(\text{C}_2\text{H}_5)\text{C}_6\text{H}_5$.—To prepare the ethyl anilide of cinnamic acid, pure, distilled cinnamyl chloride was gradually added to an excess of ethyl aniline. The reaction which took place in the cold was completed by warming for an hour on a water-bath. The resulting oil was poured into dilute hydrochloric acid, the insoluble portion dissolved in ether, and the ethereal solution washed with dilute hydrochloric acid and with a dilute solution of sodium carbonate. The ether, on evaporation, left a greenish-yellow oil that solidified on standing. The solid was purified by recrystallization from low-boiling ligroin. It may also be purified by solution in ether and precipitation with ligroin,

but has a strong tendency to separate from solution as an oil. From ligroin it crystallizes in large colorless prisms that melt at 74° . It is readily soluble in ether, alcohol, chloroform, and carbon bisulphide; moderately soluble in boiling ligroin. An analysis gave the following results:

0.1280 gram substance gave 0.5409 gram CO_2 and 0.1117 gram H_2O .

	Calculated for $\text{C}_{17}\text{H}_{17}\text{ON}$.	Found.
C	81.28	81.05
H	6.77	6.82

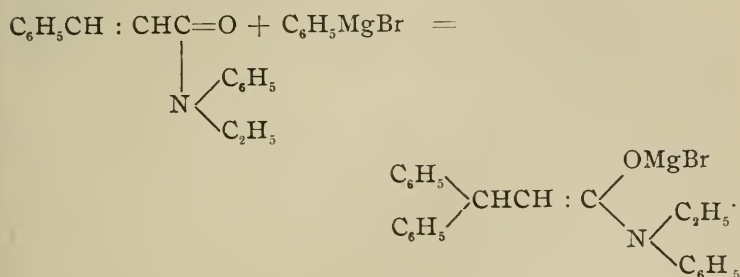
Diphenylpropionethyl Anilide,



cinnamic acid ethyl anilide was added, drop by drop, to a solution of phenylmagnesium bromide, each drop produced a white precipitate, which rapidly disappeared on shaking, until the liquid contained almost 1 molecule of the anilide for each atom of magnesium that was used in the preparation of the magnesium compound. As soon as the precipitate no longer disappeared on shaking, the mixture was poured into iced hydrochloric acid, and the product of the reaction isolated in the usual way. The result was an oil that could not be obtained in solid form. The oil contained nitrogen, and the products of hydrolysis show that, for the most part at least, it was the ethyl anilide of β,β -diphenylpropionic acid.

For the purpose of hydrolysis, 20 grams of the oil were heated at 150° , for eight hours, with concentrated hydrochloric acid. The contents of the tube were then diluted with water and extracted with ether. The ether, on evaporation, left 12.5 grams of an acid that melted sharply at 150° after one recrystallization from dilute alcohol, and was β,β -diphenylpropionic acid. The aqueous solution from which the acid had been removed was evaporated to dryness, the green residue dissolved in water, the solution made alkaline with potassium hydroxide, and distilled in a current of steam. Ethyl aniline, boiling

at 195°, passed into the distillate. The 12.5 grams of acid correspond to 90 per cent of diphenylpropion ethyl anilide. At least 90 per cent of the original anilide, therefore, reacted according to the equation :



The magnesium compound that is formed has the same general properties as those magnesium compounds obtained from esters by the same reaction. When decomposed with water or acids the product is the ethyl anilide of a saturated acid. On treatment with bromine it gives a brom substitution-product of this anilide, as shown by the following experiment :

An ethereal solution of 25 grams of cinnamyl ethyl anilide was added to a solution of phenylmagnesium bromide, obtained by dissolving 2.6 grams of magnesium in 18 grams of brombenzene. After boiling the mixture for half an hour it was cooled in a freezing-mixture and treated with bromine that had been distilled from phosphorus pentoxide. The bromine was added very slowly, from a dropping-funnel, until the red color of the liquid showed a slight excess. The thick, pasty liquid obtained in this way was immediately poured into water. The ethereal layer was separated, washed with dilute sodium carbonate until colorless, and dried with sodium sulphate. On evaporating the ether, a solid separated in large, lustrous prisms. The substance was purified by recrystallization from alcohol until the melting-point remained constant at 178°. An analysis gave the following results :

0.1632 gram substance gave 0.4039 gram CO_2 and 0.0819 gram H_2O .

	Calculated for $C_{23}H_{29}ONBr$.	Found.
C	67.65	67.49
H	5.40	5.58

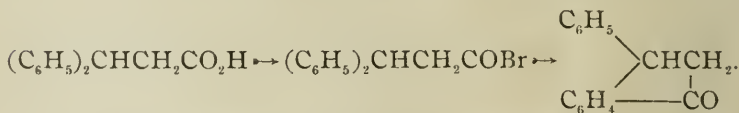
Diphenylbromopropion ethyl anilide crystallizes in large, colorless prisms. It is readily soluble in chloroform, acetone, and boiling alcohol; moderately in ether and cold alcohol; sparingly in ligroin.

Diphenylbromopropionic acid, $(C_6H_5)_2CH.CHBrCO_2H$, was obtained by hydrolyzing the ethyl anilide with concentrated hydrochloric acid in a sealed tube. It was purified by recrystallization from a mixture of ether and ligroin. The analysis gave the following results:

0.1485 gram substance gave 0.3203 gram CO_2 and 0.0601 gram H_2O .

	Calculated for $C_{15}H_{13}O_2Br$.	Found.
C	59.01	58.81
H	4.26	4.50

The acid is readily soluble in alcohol and in ether, sparingly in ligroin, insoluble in water. It melts with decomposition at about 164° . When boiled with alcoholic potash it slowly loses hydrobromic acid and passes into β -phenylcinnamic acid. As this is the easiest way of getting β -substituted cinnamic acids, an effort was made to prepare the brom acid by direct bromination of diphenylcinnamic acid by the Hell-Volhard-Zelinsky method, but it was found that the acid bromide, which is formed intermediately, so easily undergoes internal condensation that the main product invariably is phenylhydrindone:



β -Phenylcinnamic Acid, $(C_6H_5)_2C : CHCO_2H$.—An alcoholic solution containing 10 grams of diphenylbromopropionic acid was boiled for four hours with an excess of potassium hydroxide. The solution was poured into water, the alcohol removed

by distillation, and the aqueous solution concentrated on the water-bath and acidified. The solid acid that separated was free from bromine. The yield was good—7 grams instead of 7.3 grams calculated—and the product almost pure, as one recrystallization from aqueous alcohol gave a substance melting sharply at 142° . The analysis gave the following results:

0.1206 gram substance gave 0.3547 gram CO_2 and 0.0594 gram H_2O .

	Calculated for $\text{C}_{15}\text{H}_{12}\text{O}_2$.	Found.
C	80.35	80.25
H	5.35	5.50

β -Phenylcinnamic acid crystallizes in colorless needles. It is readily soluble in alcohol and in ether, moderately in boiling water, sparingly soluble in ligroin. It does not combine with bromine at ordinary temperatures, but instantly reduces cold solution of potassium permanganate. The products of oxidation are benzophenone, carbon dioxide, and water.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
August, 1904.

THE REACTION BETWEEN ORGANIC MAGNESIUM COMPOUNDS AND UNSATURATED COMPOUNDS.

III. REACTIONS WITH COMPOUNDS CONTAINING BROMINE.

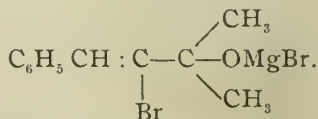
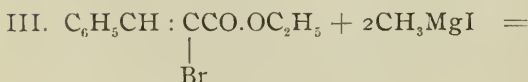
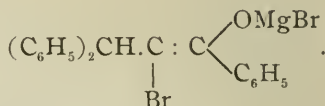
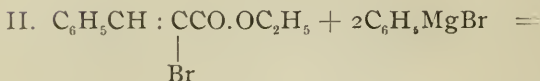
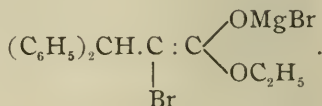
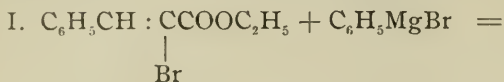
By E. P. KOHLER AND RUTH M. JOHNSTIN.

The principal object of the experiments described below was to ascertain to what extent the reactions considered in previous papers¹ are influenced by the presence of halogen atoms in the α -position. Incidentally we also studied the reaction between organic magnesium compounds and some dihalogen compounds obtained by the addition of bromine to α,β -unsaturated acids and α,β -unsaturated ketones.

We have found that the presence of a halogen atom in the α -position does not materially affect the primary reaction between organic magnesium derivatives and unsaturated com-

¹ This JOURNAL, 31, 642; 33, 21.

pounds. This is clear from the reactions of α -bromcinnamic ester, as illustrated by the following equations :

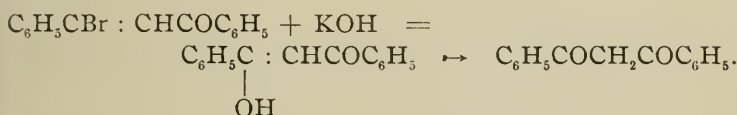


All these reactions are exactly like the corresponding ones with cinnamic ester. The α -halogen atom, however, diminishes the tendency to form secondary products. With α, β -unsaturated esters and α, β -unsaturated ketones that have hydrogen in the α -position, secondary reactions invariably take place unless the magnesium compound is in large excess and the reaction is carried out in a freezing-mixture. With α -brom substitution-products of these substances the reactions can be carried out at the ordinary temperature, and, if the magnesium compound is in sufficient excess, even at the boiling-point of ether, without fear of secondary products.

It will be seen that we regard brombenzalacetophenone as an α -substitution-product although, hitherto, it has always been regarded as a β -bromketone. The substance was first made by Wislicenus and Schmidt,¹ by eliminating 1 molecule

¹ Ann. Chem. (Liebig), 308, 219.

of hydrobromic acid from benzalacetophenone bromide. This reaction would certainly be expected to give an α -bromketone, because in all cases in which hydrobromic acid has been eliminated from an α,β -dibrom aldehyde, acid, or ester, the result has been an α -brom derivative. Wislicenus and Schmidt give no reasons for assuming a different result in the case of benzalacetophenone bromide, but their formula was evidently based on the following transformation. By boiling the bromide with alcoholic potash they obtained dibenzoylmethane and a substance which they regarded as either an enol modification of ordinary dibenzoylmethane or else a stereoisomer of that substance, which may itself be an enol modification. Assuming that these compounds were obtained as a result of direct replacement of bromine, they represented the reaction by the equation :



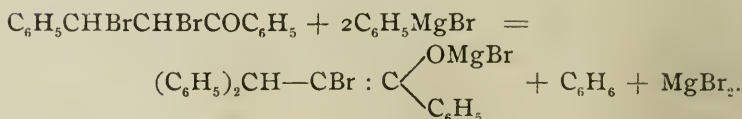
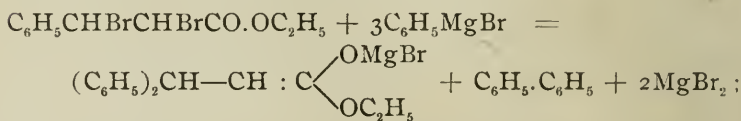
Quite recently Ruhemann and Watson¹ have found that the substance obtained by the action of potassium hydroxide on brombenzalacetophenone does not have the composition of dibenzoylmethane, but that of an ethoxyl compound containing ethoxyl in place of bromine. Ruhemann and Watson retain the earlier formula for the bromketone and assume that the ethoxyl compound is formed either by direct replacement of bromine, or by preliminary loss of hydrobromic acid and subsequent addition of alcohol to the resulting acetylene ketone. There can be no doubt that the ethoxyl compound is a β -substitution-product of benzalacetophenone, but neither this nor any other reaction that involves the elimination of the bromine atom can be used to determine the structure of the brom ketone. It is well known that in compounds having halogen in combination with doubly linked carbon it is easier to eliminate the halogen as a halogen acid than to replace it. It seems probable, therefore, that in all transformations of these substances in which the halogen is apparently substituted, the

¹ J. Chem. Soc., 85, 456.

product that is obtained is, in reality, the result of addition to an acetylene compound, formed by loss of halogen acid from the ethylene derivative. In accordance with a well-known rule, this product will always be a β -derivative. Moreover, Moureu and Brachin¹ have found that, in the presence of alkalis, acetylene ketones readily combine with alcohols to form β -alkoxyl derivatives of ethylene ketones.

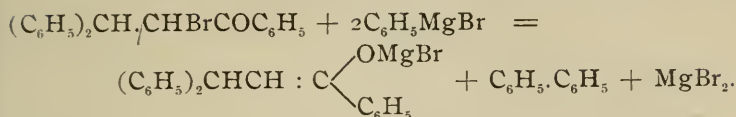
Our evidence as to the structure of brombenzalacetophenone seems conclusive. Phenylmagnesium bromide combines with α -bromcinnamic ester to form a magnesium compound which, when decomposed with water, gives diphenylbromopropiophenone, in which the bromine must be in the α -position. The same bromketone is obtained when the addition-product of phenylmagnesium bromide and brombenzalacetophenone is decomposed with water. The bromine in brombenzalacetophenone must, therefore, also be in the α -position.

The experiments with dihalogen compounds were made in the hope that it might be possible to get unsaturated tertiary alcohols, like diphenylstyrylcarbinol, indirectly, by first making the corresponding dihalogen compounds and subsequently removing bromine. It was found, however, that the magnesium compounds invariably eliminate either hydrobromic acid or bromine and subsequently combine, in the usual way, with the resulting unsaturated compounds. Two typical reactions are illustrated by the following equations:



The unsaturated magnesium compound is formed even when the ketone contains but one halogen atom:

¹ Chem. Ztg., 28, 731.



EXPERIMENTAL.

I. Reactions with Unsaturated Compounds.

Phenylmagnesium Bromide and Ethyl α -Bromcinnamate.—An ethereal solution of 27 grams of the ester was added, gradually, to a solution of phenylmagnesium bromide, obtained by dissolving 5 grams of magnesium in 33 grams of brombenzene and 100 grams of ether. As soon as the yellow precipitate that first formed had completely disappeared the liquid was poured into ice-water and the product separated in the usual way. On evaporating the ether, nearly one-third of the product separated as a solid; the rest remained liquid even when cooled in a freezing-mixture. The solid was purified by solution in chloroform and precipitation with absolute alcohol. It melted at 163° , and was found to be the same diphenylbromopropiophenone that had previously been obtained by treating benzalacetophenone with phenylmagnesium bromide and bromine.¹

The liquid containing the rest of the product was boiled for several hours with alcoholic potash. After evaporating the alcohol there remained a mixture of potassium bromide and potassium salts of organic acids that was almost completely soluble in water. The water solution was first extracted with ether to remove a small quantity of colored substances, then acidified with dilute acid. The organic acids were precipitated as an oil that solidified almost immediately. The solid was evidently a mixture of low- and high-melting acids. By fractional crystallization from water it was ultimately separated into benzoic acid, melting at 124° , and β -phenylcinnamic acid, melting at 155° . The nature of the latter acid was established by analysis and by oxidation. The analysis gave the following results:

0.1097 gram substance gave 0.3225 gram CO_2 and 0.0540 gram H_2O .

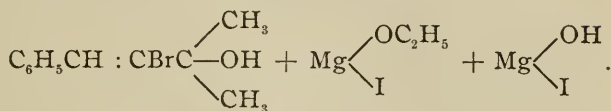
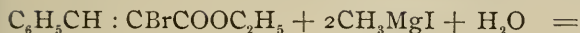
¹ This JOURNAL, 31, 652.

	Calculated for $C_{16}H_{12}O_2$.	Found.
C	80.35	80.54
H	5.35	5.60

The acid reduced alkaline permanganate solution in the cold, being oxidized to benzophenone, carbon dioxide and water.

The products obtained from the reaction are accounted for as follows : A part of the ester (about 70 per cent) combines directly with phenylmagnesium bromide. When the resulting magnesium compound is decomposed with water it gives α -brom- β,β -diphenylpropionic ester ; on boiling with alcoholic potash this passes into β -phenylcinnamic acid by hydrolysis and loss of hydrobromic acid. The rest of the ester reacts with phenylmagnesium bromide to form brombenzalacetophenone, which immediately combines with a second molecule of the bromide ; when the resulting magnesium compound is decomposed with water it forms α -brom- β,β -diphenylpropionophenone.

Methylmagnesium Iodide and Ethyl α -Bromcinnamate.—The reaction was carried out like that with phenylmagnesium bromide. The oily product contained no ester because no alcohol was obtained by boiling it with concentrated aqueous potassium hydroxide. It was slowly decomposed by boiling alcoholic potash, the products being potassium bromide, potassium benzoate, and a gum. The nature of the product was established by oxidation. A dilute solution of potassium permanganate was slowly added to the oil suspended in ice-water. As soon as the permanganate was no longer decolorized as fast as added, the liquid was distilled in a current of steam. The distillate contained acetone, because it gave dibenzalacetone when allowed to stand with benzaldehyde and a few drops of sodium hydroxide. From the residue left in the distilling flask we obtained benzoic acid and a small quantity of a very soluble, low-melting acid, which could not be identified with certainty, but which was probably oxyisobutyric acid. These oxidation-products indicate that the main product of the reaction was a tertiary alcohol :



Phenylmagnesium Bromide and α -Brombenzalacetophenone.—

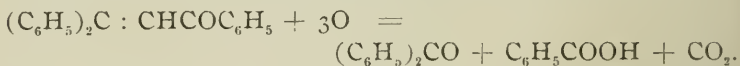
An ethereal solution of 28 grams of the ketone was added to a solution obtained by dissolving 5 grams of magnesium in 33 grams of brombenzene mixed with absolute ether. The reaction was carried out at the temperature of boiling ether. The yellow precipitate that separated immediately redissolved and the solution was poured into ice-water as soon as all the ketone had been added. Almost the entire product was deposited from the ether as a crystalline solid. The remainder was obtained by evaporating the residue on the water-bath. After one recrystallization from acetone the compound melted at 163° , the melting-point of pure α -brom- β,β -diphenylpropiophenone. The reaction was a perfectly clean one. The yield was 35 grams of pure bromdiphenylpropiophenone instead of 36.6 grams calculated.

Phenylbenzalacetophenone, $(\text{C}_6\text{H}_5)_2\text{C} : \text{CHCOC}_6\text{H}_5$. — When bromdiphenylpropiophenone is boiled with alcoholic potash it slowly loses hydrobromic acid. Twenty-four grams of the ketone were boiled with a solution of 3.5 grams of potassium hydroxide in absolute alcohol. The solution soon became bright yellow in color and potassium bromide separated on the walls of the flask. After boiling for six hours the alcohol was removed by distillation and the residue poured into water. The heavy oil, that remained after the removal of potassium bromide, was dissolved in ether, the ethereal solution dried with sodium sulphate, and the ether evaporated. The product again separated as an oil but this solidified on standing. The yellow solid was recrystallized from alcohol until the melting-point remained constant at 92° . An analysis gave the following results :

0.2011 gram substance gave 0.6534 gram CO_2 and 0.1045 gram H_2O .

	Calculated for $C_{21}H_{16}O$.	Found.
C	88.70	88.61
H	5.61	5.77

The ketone crystallizes from alcohol in large, lemon-yellow prisms. It is readily soluble in alcohol and in ether, slightly soluble in ligroin. The solution in concentrated sulphuric acid is yellow at first, but rapidly turns to a deep red color. Water reprecipitates the original substance. The structure of the compound was established by oxidation. For this purpose 4 grams of the ketone were suspended in dilute solution of sodium carbonate, contained in a distilling-flask that was connected with a condenser and a steam generator. From a dropping-funnel dilute solution of potassium permanganate was slowly added, while a rapid current of steam was passed through the boiling liquid. A colorless oil collected in the receiver. This solidified when touched with a crystal of benzophenone, the resulting solid melting at 56° , the melting-point of pure benzophenone. The contents of the distilling-flask were filtered, the filtrate evaporated to small volume and acidified. The solid that separated was benzoic acid and the liquid contained no other organic substance. The original compound was, therefore, β -phenylbenzalacetophenone :

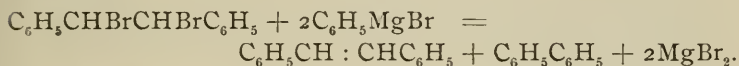


This is, doubtless, the easiest way of making ketones of this type.

II. Reactions with Saturated Halogen Compounds.

Phenylmagnesium Bromide and Stilbene Bromide.—Seventeen grams of finely powdered stilbene bromide were added to a solution obtained by dissolving 5 grams of magnesium in bromobenzene and absolute ether. The substances react quietly at the ordinary temperature. After boiling for a short time to complete the reaction, the mixture was poured into dilute hydrochloric acid. The ethereal layer was separated and distilled in a current of steam as long as an oil, that solidified in the condenser, was carried over freely. The solid in the dis-

tillate was filtered off and crystallized from ligroin. It gave 7.8 grams of pure diphenyl. The residue in the distilling flask was recrystallized from alcohol and yielded 8 grams of stilbene. The reaction evidently takes place smoothly, according to the equation :



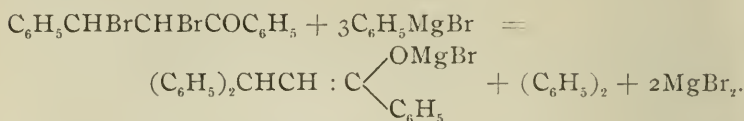
Phenylmagnesium Bromide and Dibromophenylpropionic Ester.

—The reagents were brought together in ethereal solution, the temperature being kept below -15° in a freezing-mixture. After standing for five hours the product was treated in the usual way. The ethereal solution, on evaporation, left an oil that partially solidified on standing. The solid was found to be diphenylpropiophenone. The part of the product that did not solidify on standing was free from bromine. It was boiled with alcoholic potash for four hours. The residue, after removing the alcohol, was completely soluble in water. From this solution hydrochloric acid precipitated diphenylpropionic acid. Hence it is clear that the first reaction which occurs is exactly like that between phenylmagnesium bromide and stilbene bromide. The magnesium compound removes the two bromine atoms, leaving ethyl cinnamate. This subsequently reacts with more of the bromide and forms the magnesium compounds which give diphenylpropionic ester and diphenylpropiophenone when they are decomposed with water.

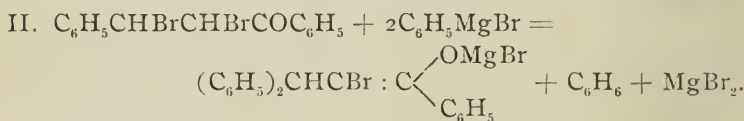
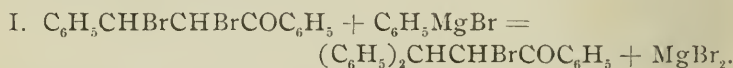
Phenylmagnesium Bromide and Benzalacetophenone Bromide.

—The result of this reaction depends, to some extent, upon the temperature. In the first experiment the finely powdered ketone was added, very slowly, to a solution of the magnesium compound that was cooled in a freezing-mixture. On pouring the mixture into iced hydrochloric acid most of the product separated in colorless crystals. After purification, by recrystallization from acetone, the solid melted at 163° —the melting-point of bromdiphenylpropiophenone. The ethereal solution, containing the rest of the product, was evaporated in a current of air and the solid residue recrystallized from alcohol. It was

composed mainly of diphenylpropiophenone mixed with a small quantity of bromdiphenylpropiophenone. The reaction was also carried out at the temperature of boiling ether. The product thus obtained was free from bromine. It was composed of diphenyl, which was removed by distillation with steam, and diphenylpropiophenone. The reaction takes place smoothly, according to the equation :



The bromketone obtained when the substances react at low temperatures might be formed either by direct replacement of bromine by phenyl I., or by elimination of hydrobromic acid and subsequent addition II.



If the reaction had taken place as represented in I., the monobromketone would have been formed before the product was decomposed with water. This was not the case because no further reaction took place when a large excess (4 mols.) of phenylmagnesium bromide was added to the mixture, while, as shown below, bromdiphenylpropiophenone instantly reacts with phenylmagnesium bromide. The product must, therefore, be a magnesium compound that gives the bromketone when it is decomposed with water.

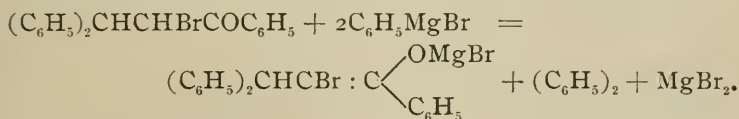
Benzalacetophenone Bromide and Naphthylmagnesium Bromide.—The solid ketone was added to an ethereal solution of α -naphthylmagnesium bromide that was cooled with running water. The product solidified when it was poured into iced hydrochloric acid and was purified by recrystallization from alcohol. An analysis gave the following results :

0.1899 gram substance gave 0.6213 gram CO_2 and 0.1024 gram H_2O .

	Calculated for $\text{C}_{25}\text{H}_{20}\text{O}$.	Found.
C	89.22	89.28
H	5.99	6.20

The solid is naphthylphenylpropiophenone because the same substance was obtained by treating benzalacetophenone with α -naphthylmagnesium bromide. The ketone is readily soluble in ether and in alcohol. It crystallizes in needles, melting at 121° .

α -Bromdiphenylpropiophenone and Phenylmagnesium Bromide.—Although bromdiphenylpropiophenone is almost insoluble in ether, it readily dissolves in an ethereal solution of phenylmagnesium bromide. The liquid becomes warm and in a short time all the bromketone disappears. The products of the reaction were separated in the usual way and were found to be diphenylpropiophenone and diphenyl. The final result is, therefore, the replacement of bromine by hydrogen. The diphenylpropiophenone is, however, not formed until the mixture is treated with water, because the result is the same when a large excess of phenylmagnesium bromide is used, while diphenylpropiophenone readily reacts with the bromide to form a tertiary alcohol. If the mixture is treated with benzoyl chloride before it is decomposed with water the product is benzoyl-triphenylpropenol. This shows that the reaction takes place according to the equation :



CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
September, 1904.

A METHOD FOR THE DETERMINATION OF THE
AFFINITIES OF ACIDS COLORIMETRICALLY,
BY MEANS OF CERTAIN VEGETABLE
COLORING MATTERS.

BY J. H. KASTLE.

The bleaching of colored flowers, such as the rose and red geranium, by means of sulphur dioxide, is one of the best known reactions of which the latter substance is capable, and it is a matter of common observation that flowers thus bleached frequently regain their original color, in part at least, if, after bleaching, they are allowed to stand for some time in contact with the air. The most obvious explanation of this phenomenon is that the sulphur dioxide, by its reducing action, produces a leuco-compound which is reoxidized on exposure to the air. It occurred to me that possibly these leuco-compounds, if really formed, could be used advantageously in measuring such oxidations as are usually brought about by the oxidases. Accordingly, several years ago, the attempt was made to employ an aqueous extract of the red geranium, that had been bleached by sulphur dioxide, as a reagent for detecting the presence of oxidizing ferments and roughly measuring their relative oxidizing powers. These earlier experiments led to no noteworthy results and after a time were discontinued. Recently the subject was taken up again in connection with some other work and it appeared that possibly the difficulties had arisen from the use of an insufficiently highly colored substance for the preparation of the leuco-compound. Accordingly, some new experiments were undertaken, using the red substance of the purple grape, the Ives Seedling variety. An aqueous extract of this was obtained by macerating the hulls of the ripe grape with water and boiling. After filtering, a dark purplish-red solution was obtained. On adding a very small amount of hydrochloric acid to this solution and shaking with zinc dust, it was speedily decolorized. On standing in a loosely stoppered test-tube the upper layers of liquid gradually regained their color. As in the case of the coloring matter of the geranium, this seemed to indicate that, in the presence of

small amounts of acid, zinc dust can reduce the red coloring matter of the grape to the corresponding leuco-compound, which is again oxidized on exposure to the air. In order to determine whether this colorless solution could be oxidized by means of oxidizing ferments, small amounts of the solution were mixed with an active extract of *lepiota Americana*, a fungus which I have found to contain a very powerful and relatively stable oxidase. It was observed that the boiled extract of the fungus produced the same amount of colored substance as its active preparations. It was also found that active extracts of the fungus, after mixing with the solution of the leuco-compound obtained from the grape, failed to give the guaiacum reaction. It was evident, therefore, that the production of the red coloring matter of the grape from the leuco-compound was not the result of oxidation, but was in some way dependent on the degree of acidity of the solution, as it was found that the intensity of the red coloration could always be greatly increased by the addition of small amounts of hydrochloric acid. A comparison of hydrochloric and acetic acids, of the same concentration, showed that, whereas the tube containing the hydrochloric acid became deep wine-red in color, that containing an equal amount of acetic acid remained practically colorless, or at most showed only faint traces of pink. This difference in the conduct of these two acids proved so striking as to suggest that the solution of the leuco-compound obtained from the purple grape could be employed in determining the affinities of acids colorimetrically.

Preparation of the Reagent.

The best method of preparing the leuco-reagent consists in macerating the hulls of the grape with water, boiling, and filtering. In order to further clarify the filtrate a small amount of a solution of egg albumen is added. After boiling and filtering a second time a perfectly clear, dark plum-red solution is obtained. A rapid current of sulphur dioxide is then passed into this liquid, which quickly becomes lighter in color, until, finally, a light salmon-pink solution is obtained which is boiled to remove the excess of sulphur dioxide. During the boiling

the color darkens but fades on cooling, leaving the solution of a very faint pink tint; a little toluene is added and the liquid protected from air. Thus prepared the solutions are quite stable and may be kept for weeks and probably longer, without undergoing change.

In studying the effect of various acids on the reagent, 1 cc. of the N/10 acid was mixed with 1 cc. of the reagent. Acids having an affinity approximately equal to that of hydrochloric acid, gave immediately a dark wine-red color, whereas weaker acids yielded a pink one, which varied in depth and tint according to the affinity of the acid employed. A comparison of the color produced with the acid under investigation and that obtained with hydrochloric, oxalic, formic and acetic acids, as standards of comparison, readily permitted the determination of its relative affinity. The color comparisons were made in small, thin-wall test-tubes of the same internal diameter. Heretofore all measurements have been made on N/10 acids, except in one or two instances.

Hydrochloric, benzene sulphonic, sulphuric, oxalic, formic, acetic, and butyric acids were the first to be tested. On mixing 1 cc. of each of these acids, in N/10 solution, with 1 cc. of the reagent the following results were obtained:

Acid.	Color of the solution.
Hydrochloric	Dark wine-red
Benzene sulphonic	" "
Sulphuric	" " lighter than two preceding
Oxalic	Dark pink, lighter than sulphuric
Formic	Pink, lighter than oxalic
Acetic	Very light pink
Butyric	" " "
Water	Trace of pink

At this dilution and with these amounts of substances, acetic and butyric acids and water gave very nearly the same shade of color, but it was very easy to distinguish formic acid from any of these and to see that the acids stood in the following order of strength:

Hydrochloric = benzene sulphonic > sulphuric > oxalic >
formic > acetic = butyric.

The reagent possesses the further advantage that the colors produced with acids are permanent, showing no tendency to fade but persisting for hours and even days, unchanged.

Succinic, Malic and Tartaric Acids.

A comparison was made of the three related acids, succinic, malic and tartaric, in the manner described above :

Acid.	Color of the solution.
Tartaric	Deep pink
Formic	Pink
Malic	Light pink
Succinic	Very light pink

After standing twenty-four hours the color of the several tubes was essentially unchanged. Formic acid was included in this series for the sake of comparison. It is evident that the following relation obtains as to the order of strength of these acids :

Tartaric > formic > malic > succinic.

Propionic and Lactic Acids.

Propionic and lactic acids were next compared in the same manner :

Acid.	Color of the solution.
Lactic	Light pink, lighter than formic, darker than malic
Propionic	Very light pink, lighter than succinic

From the color comparison in the case of these two acids there can be no doubt that lactic acid is considerably stronger than propionic, and that the latter belongs to the class of very weak acids, such as acetic and butyric.

Acetic, Monochloracetic, and Trichloracetic Acids.

Acetic, monochloracetic, and trichloracetic were the next acids compared, using hydrochloric, oxalic and formic acids as standards :

Acid.	Color of the solution.
Hydrochloric	Dark wine-red
Trichloroacetic	Wine-red, lighter than hydrochloric
Oxalic	Deep pink
Monochloroacetic	Pink, lighter than oxalic
Formic	" " " mono-chloroacetic
Acetic	Very light pink

These acids therefore stand in the following order of affinity :

Hydrochloric > trichloroacetic > oxalic > monochloroacetic > formic > acetic.

Nitric, Hydrobromic, Iodic, and p-Nitrotoluene Sulphonic Acids.

These acids were compared with hydrochloric :

Acid.	Color of the solution.
Hydrochloric	Dark wine-red
Nitric	" "
Hydrobromic	" "
p-Nitrotoluene sulphonic	" "
Iodic	Yellow

It will be observed that nitric, hydrobromic, and *p*-nitrotoluene sulphonic acids are equal to hydrochloric acid in their affinity. The yellow color produced by the iodic acid is due to the liberation of iodine by the action, on the iodic acid, of the small amount of sulphur dioxide remaining in the reagent. Its exceptional conduct is thus readily accounted for.

Citric and Meconic Acids.

Citric and meconic acids were compared, using hydrochloric, formic, and acetic as standards :

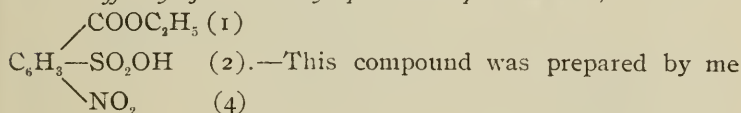
Acid.	Color of the solution.
Citric	Pink
Formic	"
Acetic	Very light pink

It is evident, therefore, that citric acid is stronger than acetic and that it is equal to, or possibly a little stronger than formic acid.

It was found impossible to prepare a N/10 solution of meconic acid in the cold, owing to its sparing solubility. Accord-

ingly, a saturated solution of the acid, in the cold, was prepared and titrated with N/10 sodium hydroxide. Ten cc. of the solution required 6.35 cc. N/10 sodium hydroxide for neutralization. In order to determine its effect on the reagent and to compare it with hydrochloric acid, two tubes were set up. Tube 1 contained 1 cc. of the solution of meconic acid and 1 cc. of the reagent. Tube 2 contained 0.635 cc. N/10 hydrochloric acid, 0.365 cc. of water, and 1 cc. of the reagent. Both tubes at once developed a dark wine-red color; the result of two comparisons showed the tube containing the meconic acid to be distinctly darker in color than that containing the hydrochloric acid. Ostwald states that meconic acid is conspicuous by its great strength. It is the strongest of all acids that consist only of carbon, hydrogen, and oxygen, and approaches very near to sulphuric acid in degree of affinity.

The Affinity of Acid Ethyl p-Nitrosulphobenzoate,



several years ago and was described as a strong acid.¹ So far as I am aware, no one has ever attempted to determine its affinity. If the compound owes its acidity to the existence of the sulphonic acid group in its molecule, it should have an affinity practically equal to that of hydrochloric acid, because the other groups in the compound are either inert or of an electronegative character. It seemed of interest to determine the affinity of this acid by means of the new reagent. A solution of the acid, of such concentration that 10 cc. required 6.15 cc. of N/10 sodium hydroxide to neutralize, it was compared with hydrochloric acid as before.

Tube No. 1 contained 1 cc. of the solution of the acid ester of *p*-nitrosulphobenzoic acid, and 1 cc. of the reagent.

Tube No. 2 contained 0.615 cc. of N/10 hydrochloric acid, 0.385 cc. of water, and 1 cc. of the reagent.

Both tubes developed a wine-red color at once, of the same depth and tint. It would seem, therefore, that the acid ester

¹ This JOURNAL, II, 190 (1889).

of *p*-nitrosulphobenzoic acid is as strong an acid as hydrochloric, a conclusion which is in harmony with the present view regarding the constitution of the former substance.

In the following table the acids here studied have been arranged in order of their strength, as determined by Ostwald's methods, and as determined colorimetrically according to the process here under consideration. The agreement is certainly as close as could be desired when we consider the great diversity of the means employed.

Table I.—Acids Arranged in Order of Their Strength.

According to Ostwald's methods.	Colorimetrically.
Hydrochloric	Hydrochloric
(Nitric) ¹	(Nitric)
(Hydrobromic)	(Hydrobromic)
(Benzene sulphonie)	(Benzene sulphonie)
	(Meconic)
	(<i>p</i> -Nitrotoluenesulphonie)
	(Acid ethyl <i>p</i> -Nitrosulphobenzoate)
Trichloracetic ²	Trichloracetic
Sulphuric	(Sulphuric)
Meconic	
Oxalic	Oxalic
Monochloracetic	Monochloracetic
Tartaric	Tartaric
Citric	Citric
Formic	Formic
Malic	Lactic ³
Lactic	Malic
Succinic	Succinic
Acetic	Acetic
Propionic	(Propionic)
Butyric	(Butyric)

Hitherto it has not been found possible to recognize the difference in strength between the very weak acids, such as

¹ The sign of parenthesis enclosing the names of certain of the acids is intended to signify that the acids so enclosed have the same affinity as the acid immediately preceding.

² According to one of Ostwald's methods trichloracetic acid is weaker than sulphuric, whereas according to two of them it is stronger.

³ According to one of Ostwald's methods lactic acid is stronger than malic, whereas according to two of them it is weaker.

acetic, propionic, and butyric, by this colorimetric method ; however, these differences are only slight. By varying the concentration it may prove possible to exhibit them.

Other Vegetable Coloring Matters as Indicators of the Degree of Acidity.

The following plants have been examined for coloring matters similar to that of the purple grape : The red-leaved achyranthes, the flower of the scarlet geranium, the flower of the purple petunia, the beet (*beta vulgaris*), poke berries (*phytolacca decandra*), the wild grape (*vitis vulpina*), the purple morning glory (*ipomœa purpurea*), the scarlet sage (*salvia fulgens*), and the cultivated red rose.

Some of the flowers of the red geranium were crushed with water and the mixture boiled and filtered. The filtrate was found to have a dull rose-red color. It was then saturated with sulphur dioxide, after which a small quantity of a solution of egg albumen was added and the liquid boiled to expel the excess of sulphur dioxide and coagulate the albumen. A clear, practically colorless solution was thus obtained. With N/10 solutions of the strong acids, such as hydrochloric, hydrobromic and nitric, this solution gave, at first, delicate shades of pink, which finally changed to orange-yellow. Acids of the strength of oxalic gave a decided salmon-pink, formic acid a very faint pink color and acetic acid no color at all. Ten acids gave the following results :

Acids.	Color of the solution.
Hydrochloric	Orange-yellow
Hydrobromic	" "
Nitric	" "
Benzene sulphonic	" "
Sulphuric	Orange-yellow, with pink tint
Meconic,	Orange-yellow, with sal- mon-pink tint
Oxalic	Salmon-pink
Formic	Faint pink
Acetic	Very faint pink
Butyric	Colorless

We should, therefore, have to arrange these acids in the following order of strength :

Hydrochloric = hydrobromic = nitric = benzenesulphonic > sulphuric > meconic > oxalic > formic > acetic > butyric.

The effect of heat is to intensify the color produced by weak acids on this solution, as seen from the following :

Acid.	Color of the solution.	
	Ordinary temperature.	100° C.
Hydrochloric	Orange-yellow	Orange-yellow
Formic	Light pink	Salmon-pink
Butyric	Colorless	Pink

It will be observed that the change produced by heat is greater for weak acids, such as formic and butyric, than it is for strong ones, such as hydrochloric. On cooling, the reverse change occurs, that is, the solutions tend to regain their original color. This reverse change, however, is incomplete, because the solutions that have once been heated are, on cooling, always a little darker than they were before heating. After heating and standing six hours, butyric acid, for example, showed a very faint pink color, whereas in the cold the solution is colorless.

Some experiments were next tried with the purple petunia. The flowers of this plant are deep plum-red in color. By maceration with water they gave a deep purplish-red solution which faded considerably on boiling, so that finally a magenta-red liquid was obtained. Sulphur dioxide rapidly changed the color to a pink and after boiling to remove the excess of gas and filtering, a yellow solution was obtained. With N/10 solutions of the strong acids, such as hydrochloric, nitric, etc., this liquid gave a faint pink coloration ; with the weaker ones, such as formic and acetic, no change of color was observable. On heating the solutions containing the strong acids, the color darkened rapidly, finally becoming deep rose-red. Oxalic acid also produced a rose-red color, lighter than that with hydrochloric acid. The solution containing formic acid developed a pink color, while the tubes containing acetic acid and water remained colorless, even after heating. On cooling, the solutions containing hydrochloric, nitric and hydrobromic acids

became deep pink, that one with oxalic acid lighter pink and the formic acid colorless. It is evident, therefore, that the coloring matter in the colored petunia can be employed, like that in the purple grape and the red geranium, for the determination of the affinities of acids colorimetrically. The acids tested with this reagent can be arranged in the following order of strength :

Hydrochloric = hydrobromic = nitric > oxalic > formic >
acetic.

The coloring matter in the flowers of the scarlet sage (*salvia fulgens*) was next tried, the flowers being macerated with water and boiled. Unfortunately, a good deal of the color was lost on boiling. After boiling and filtering, the solution was found to be purplish-red in color. It was saturated with sulphur dioxide and boiled to remove the excess of the gas. While hot it had an orange-yellow color, which, on cooling, became light-yellow. In its conduct toward acids this vegetable coloring matter was found to be very similar to that present in the red geranium. The color of the flowers of these two plants is very much alike. The following results were obtained with some of the N/10 acids :

Acid.	Color of solution, cold.	Color of solution, hot.
Hydrochloric	Salmon-pink	Orange-yellow
Hydrobromic	"	"
Nitric	"	"
Acetic	Colorless	Pink
Water	"	Very light pink

Meconic acid was compared with hydrochloric acid in the manner already described on page 50, with the following result :

Acid.	Color of the solution.
Hydrochloric	Salmon-pink
Meconic	"

In the order of their strength, therefore, these acids should be arranged as follows :

Hydrochloric = hydrobromic = nitric = meconic > acetic.

A solution of the coloring matter in the wild grape (*vitis*

vulpina), prepared and bleached with sulphur dioxide in the manner already described, was found to conduct itself towards acids in precisely the same way as the cultivated variety. With the strong acids, such as hydrochloric, nitric, etc., it gave beautiful wine-red solutions, with the weaker ones, such as formic and acetic, delicate shades of pink.

With poke berries, the purple beet, and the flowers of the purple morning glory no satisfactory results were obtained, doubtless for the reason that it was found difficult, or in some cases impossible, to bleach the coloring matters of these plants by means of sulphur dioxide. After saturating the solution with sulphur dioxide, prolonged boiling removes the color of the purple beet, with the result, however, that the coloring matter seems to be permanently destroyed. On the other hand, the coloring matters of the poke berry and the purple morning glory, while quite unstable, do not seem capable of being bleached by sulphur dioxide.

Interesting results have been obtained with the cultivated variety of the red rose. The coloring matter was extracted with cold water and the solution saturated with sulphur dioxide. A slight yellowish-pink liquid was thus obtained. With N/10 acids this solution gave the following colors :

Acid.	Color of solution, hot.	Color of solution, cold.
Hydrochloric	Deep reddish-orange	Rose-pink
Hydrobromic		"
Nitric		"
Benzene sulphonic		" darker than hydrochloric
Meconic		Rose-pink, lighter than hydrochloric
Oxalic		Very faint pink
Acetic	Pink	Colorless
Water	"	"

On cooling the hot solutions containing the acetic acid and water they became colorless and the hot solution of hydrochloric acid, which was deep reddish-orange, became rose-pink, deeper in color, however, than the solution that had remained in the cold.

Some of the solution of the coloring matter of the red rose, which had been extracted with cold water and bleached with sulphur dioxide, was boiled for a short time to expel the excess of sulphur dioxide. On cooling, the liquid was found to have a very slight yellowish color and when mixed with an equal volume of N/10 hydrochloric acid it developed a deep rose-red color at once, much deeper in fact than had been obtained with the solution before it was boiled. With the boiled solution the following results were obtained :

Acid.	Color of the solution, cold.
Hydrochloric	Deep rose-red, tending to orange
Nitric	" " " " "
Oxalic	" rose-pink, much lighter than hydrochloric
Formic	Very faint salmon-pink
Acetic	Colorless

The difference between acids equal or superior to oxalic in strength and those equal or inferior to formic is certainly distinctly brought out in these experiments.

The coloring matter of the red rose was found to dissolve readily in 95 per cent alcohol even in the cold. A small amount of this solution was allowed to evaporate spontaneously in the air, and the residue dissolved in a small quantity of water. On adding a drop or two of N/10 hydrochloric acid it became deep orange-red and much darker than it was originally. This suggested that possibly a solution of the coloring-matter of the red rose could be employed to determine the strength of acids colorimetrically, without previously bleaching with sulphur dioxide. Accordingly, an equal volume of water was added to an alcoholic solution of the coloring matter of the red rose and the mixture heated on the water-bath until all of the alcohol was removed. The aqueous solution was diluted with distilled water and divided into three portions. These were employed as follows :

1. One was boiled, with the addition of a small amount of animal charcoal, and filtered. The solution thus obtained was slightly yellowish and gave the following results with water and acids :

Acid.	Color of the solution.
Hydrochloric	Deep rose-pink
Acetic	Faint pink
Water	Colorless

2. The second portion was treated with a small amount of animal charcoal in the cold and filtered. It was found possible to remove the red color even in this way, a slightly yellowish solution resulting, which gave the following results with water and acids :

Acid.	Color of the solution.
Hydrochloric	Deep rose-pink
Acetic	Faint pink
Water	Colorless

3. The third portion of the solution was simply diluted with water until it had only a faint yellowish-pink color. With water and acids it gave the following results :

Acid.	Color of the solution.
Hydrochloric	Deep rose-pink
Oxalic	" " (only a little lighter than hydrochloric)
Formic	Light pink
Acetic	Very faint pink
Water	Colorless

From a superficial consideration of these results one might be inclined to believe that dilute solutions of the plant coloring matter could be employed directly in determining the strength of acids, without previously bleaching with sulphur dioxide. It should be observed, however, that although the color of such liquids is greatly increased by the addition of an acid and although a much deeper coloration is produced by a strong acid than by a weak one, the reagent is lacking in sensitiveness. For example, it will be seen from the results under 3 that oxalic acid produced very nearly as intense a coloration as hydrochloric acid. On the other hand, if we employ a solution of the coloring matter of the red rose that has been bleached with sulphur dioxide, the difference between hydrochloric and oxalic acid is readily perceptible, as will be seen from the results recorded on page 56.

The same is true of the purple coloring matter of the grape, namely, that the color of its solutions is markedly intensified by the addition of an acid. An aqueous extract of the hulls of the purple grape, that had been diluted until it had only a faint pink color, gave the following results on the addition of N/10 acids:

Acid.	Color of the solution.
Hydrochloric	Deep pink
Oxalic	" " (only a little lighter than hydrochloric)
Formic, tartaric, and lactic	Light pink, and not distinguishable one from the other
Acetic	Very faint pink
Water	" " " (lighter than acetic acid)

Here, again, we see that the solution lacks delicacy as compared with the solutions of the coloring matter that have been bleached with sulphur dioxide. It will be observed, therefore, that, by means of certain of the vegetable coloring matters which have been bleached by sulphur dioxide, it is possible to determine the relative affinity of acids colorimetrically, with the greatest ease and rapidity, and that the color changes are such as to render the method a beautiful one for the purposes of chemical demonstration. As to the mechanism of the reaction upon which the method is based but little is known at present. Acids are essential to the development of the color of certain dye-stuffs, such as those of the rosaniline type. If acids are required to produce the colored substance from an antecedent chromogen it is but logical to conclude that, in certain cases at least, the quantity of the colored substance actually formed and existing in the solution of the dye, and hence the intensity of the color, would depend not only on the quantity of acid present but also on the degree of its ionization.

ON DERIVATIVES OF FORMHYDROXAMIC ACID AND THE POSSIBLE EXISTENCE OF ESTERS OF FULMINIC ACID.

BY H. C. BIDDLE.

The possible existence of esters of fulminic acid,



is of interest not only on account of the isomerism of these bodies with the alkyl isocyanates, but also because of their presenting additional examples of bivalent carbon.

The extent to which the valence of an element may be varied by the nature of an attached radical is a subject of ever increasing importance. It would appear that the limits of such variation are somewhat wider than was anticipated a few years ago. The tetravalence of oxygen seems now to be established beyond dispute.¹ If the determination of the molecular complexity of a metal dissolved in mercury is a just criterion of its molecular aggregation,² the metal is apparently monatomic under such conditions, and the valence of the atoms for one another is consequently zero. The bivalence of carbon appears to obtain in such derivatives as carbon monoxide, the isonitriles³ and the fulminates. In triphenylmethyl, Gomberg⁴ has shown strong probability of the existence of trivalent carbon, and Thiele⁵ would explain the mechanism of many reactions on the assumption of a residual affinity of the carbon atom, thus ascribing to the element a potential valence of five.

The similarity in structure between the isonitriles and the esters of fulminic acid would naturally lead us to expect a close resemblance in general behavior between these two classes of bodies. Like the former, the latter would probably be characterized by an "isonitrile" odor. Being unsaturated, they should exhibit an absorptive tendency toward such bodies as the halogens. On saponification they would probably yield formic acid and the α -alkylated hydroxylamines.

¹ Baeyer and Villiger: *Ber. d. chem. Ges.*, **34**, 2679 (1901), and others; see Review, *This JOURNAL*, **27**, 311 (1902).

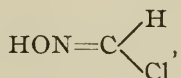
² Ramsay: *J. Chem. Soc. (London)*, **55**, 521 (1889).

³ Nef: *Ann. Chem. (Liebig)*, **270**, 267 (1892); **280**, 291 (1894); **287**, 265 (1895).

⁴ *Ber. d. chem. Ges.*, **33**, 3150 (1900); **34**, 2726 (1901); etc.

⁵ *Ann. Chem. (Liebig)*, **306**, 87 (1899).

The synthesis of such a class of bodies as the fulminic esters seems not improbable, although their preparation by the action of alkyl iodides on silver or mercury fulminate is, apparently, not feasible.¹ The properties of formyl chloride oxime,

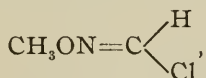


as described by Nef, suggest the possibility of eliminating hydrogen chloride from the alkyl derivatives of this body as a method for obtaining the alkyl fulminates. Some time ago, with this end in view, the benzyl, benzoyl, and acetyl derivatives of formyl chloride oxime were synthesized and their properties studied.²

Benzyl formyl chloride oxime is a body of great stability and boils, without decomposition, under atmospheric pressure, at about 210°. On treatment with alcoholic potash, however, the molecule is completely disrupted, there being formed, among other products, hydrochloric acid, ammonia, and benzyl alcohol. In this reaction there is not the slightest odor in any way resembling that of an isonitrile.

Acetyl formyl chloride oxime is a body of much less stability than the corresponding benzyl derivative. With silver nitrate it undergoes decomposition, yielding, among other products, silver fulminate.

With the thought that the methyl ester would probably afford more satisfactory results, a study of this derivative has been undertaken. Methyl formyl chloride oxime,



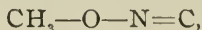
as I shall show later in this paper, is a body closely resembling the benzyl ester in stability. Its decomposition with caustic alkalis, under like conditions, appears to be less deep-seated than that of the latter. On treatment with potassium hydroxide it yields, apparently, minute quantities of a neutral, unsaturated

¹ Nef: *Ann. Chem. (Liebig)*, **280**, 339 (1894).

² *Ibid.*, **310**, 1 (1899).

body, possessing a strong isonitrile-like odor, together with other products.

That the body in question is the fulminic ester,



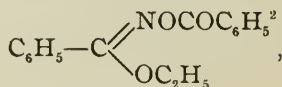
seems highly probable, though, unfortunately, the difficulty of preparing material, and the small quantity of substance obtained have thus far precluded its isolation and identification.

EXPERIMENTAL.

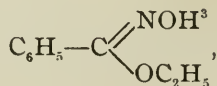
Synthesis of α -Methyl Hydroxylamine Hydrochloride, $\text{CH}_3\text{ONH}_2 \cdot \text{HCl}$.—The preparation, in quantity, of the α -alkylated hydroxylamines of the aliphatic series presents a number of difficulties. The following process, however, while quite long and tedious, affords fair yields of the methyl derivative.

Hydroxylamine hydrochloride is converted into dibenzhydroxamic acid, according to the general method suggested by Lossen.¹ The product of the reaction is allowed to stand one to two days and is then filtered, without acidifying it, as directed by Lossen.

The crude acid is purified by washing with water, digesting with hydrochloric acid and again washing with water. The yield should at least equal 80 per cent of the theory (calculating from hydroxylamine hydrochloride used). When dry, the acid is dissolved in cold baryta water (0.5 molecule $\text{Ba}(\text{OH})_2$), and is precipitated as silver salt by the addition of silver nitrate. From the silver salt are obtained, by successive steps, the ethyl ester of dibenzhydroxamic acid,



ethyl benzhydroxamic acid,

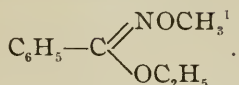


¹ Ann. Chem. (Liebig), **161**, 351 (1872).

² Eiseler: *Ibid.*, **175**, 326 (1875).

³ Eiseler: *Ibid.*, **175**, 328 (1875); **205**, 285 (1880).

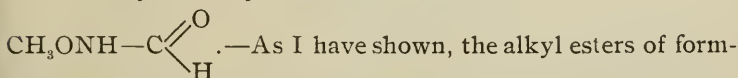
and the methyl ester of the latter,



Satisfactory results are secured by making use, in the different steps, of the crude products as they are obtained from the ether extracts, after distilling off the ether on the water-bath. On saponification with hydrochloric acid, the methyl ester of ethyl benzhydroxamic acid is readily decomposed into ethyl benzoate and methoxylamine hydrochloride.² The acid solution is evaporated to dryness on the water-bath and the crude salt purified by crystallizing it twice from alcohol and ether. From 250 grams of hydroxylamine hydrochloride 70 grams of α -methyl hydroxylamine hydrochloride are thus obtained, crystallizing in snow-white, hygroscopic leaflets, and melting at 148° to 149° .

α -Methyl hydroxylamine hydrochloride does not reduce Fehling's solution. The reducing action noted by Lossen² was doubtless due to the presence of the β -derivative, which is always formed in the above synthesis. As has been shown by Dunstan and Goulding,³ the formation of β - with α -derivatives is a normal result when alkylating the aldoximes and ketoximes in the presence of sodium alcoholates.

The Methyl Ester of Formhydroxamic Acid,



hydroxamic acid are readily obtained by heating formic acid with α -alkylated hydroxylamines.⁴

To 30 grams of α -methyl hydroxylamine hydrochloride, a concentrated solution of potassium hydroxide (1 to 2 molecules) is added and the mixture is slowly distilled into formic acid (99 per cent), the temperature of the distilling-bulb being eventually raised to 150° .

The formic acid solution is concentrated on the water-bath

¹ Lossen : Ann. Chem. (Liebig), **182**, 224 (1876) ; **281**, 216 (1894).

² Lossen and Zanni : *Ibid.*, **182**, 225 (1876).

³ J. Chem. Soc. (London), **79**, 628 (1901).

⁴ Ann. Chem. (Liebig), **310**, 9 (1899).

and is then distilled under diminished pressure. The main fraction is a colorless liquid which boils at 116° to 117° under 33 mm., at 123° to 124° under 45 mm., and at 126° to 127° under 50 mm. pressure. On standing for a short time, the liquid solidifies to a mass of colorless, prismatic crystals, melting at 38° to 39° .

On analysis the following results were obtained :

0.1952 gram substance gave 0.2284 gram CO_2 and 0.1197 gram H_2O .

0.1560 gram substance gave 25 cc. moist N at 13° .5 and 758 mm. pressure.

	Calculated for $\text{C}_2\text{H}_5\text{O}_2\text{N}$.	Found.
C	32.00	31.91
H	6.66	6.81
N	18.66	18.90

The methyl ester of formhydroxamic acid is a deliquescent substance, possessing a marked tendency to crystallize. By the action of hydrochloric acid it is decomposed into formic acid and α -methyl hydroxylamine hydrochloride. The ester is also dissociated in the presence of chlorplatinic acid, the orange-yellow plates of the platinum double salt of α -methyl hydroxylamine hydrochloride being formed.

0.1559 gram substance gave 0.0601 gram Pt.

	Calculated for $(\text{CH}_3\text{ONH}_2\cdot\text{HCl})_2\text{PtCl}_4$.	Found.
Pt	38.69	38.55

Silver Salt of the Methyl Ester of Formhydroxamic Acid.

—This salt is prepared by the addition of silver nitrate to a solution of the ester, in the calculated amount of dilute caustic sodium hydroxide. It separates in snow-white leaflets, which undergo but little change when dried *in vacuo* over sulphuric acid.

0.2338 gram substance gave 0.1842 gram AgCl .

	Calculated for $\text{C}_2\text{H}_4\text{O}_2\text{NAg}$.	Found.
Ag	59.34	59.29

When heated, the silver salt is decomposed. It reacts in the cold with acetyl and benzoyl chlorides and with methyl and

ethyl iodide, yielding the corresponding acyl and alkyl derivatives.

Action of Phenyl Isocyanate on the Methyl Ester of Formhydroxamic Acid.—Phenyl isocyanate readily reacts with the methyl ester to form an addition-product. The clear solution, resulting from gently warming an equimolecular mixture of the two substances, soon solidifies to a crystalline mass. After standing until the odor of the isocyanate has disappeared, the solid is recrystallized from chloroform and ether and is thus obtained in colorless leaflets, which melt at 123° to $123^{\circ}.5$.

0.1971 gram gave 24.3 cc. of moist N at $11^{\circ}.5$ and 753.7 mm. pressure.

	Calculated for $C_9H_{10}O_3N_2$.	Found.
N	14.43	14.58

This addition-product is difficultly soluble in ether, alcohol, and hot water, insoluble in cold water, readily soluble in chloroform. Its constitution is probably that of a urea rather than that of a urethane, although this has not as yet been determined. The solution of this question is of some interest, as it would doubtless indicate whether the original ester is to be regarded as a derivative of formhydroxamic acid, $CH_3-O-NH-CH=O$, or of formhydroximic acid, $CH_3-O-N=CH-OH$.

Methyl Formyl Chloride Oxime, $CH_3-O-N=C \begin{smallmatrix} H \\ \diagup \\ Cl \end{smallmatrix}$. — As

I have shown, benzyl formyl chloride oxime is formed by treating the benzyl ester of formhydroxamic acid with phosphorus pentachloride.¹ In like manner, methyl formyl chloride oxime may be obtained from the methyl ester of formhydroxamic acid.

Ten grams of the methyl ester of formhydroxamic acid are well cooled and treated slowly with 27.7 grams of phosphorus pentachloride (1 molecule). The reaction begins immediately, with evolution of hydrogen chloride. When the product has become a homogeneous yellow liquid, it is carefully

¹ Ann. Chem. (Liebig), **310**, 11 (1899).

distilled, the temperature of the distilling bulb not being allowed to rise above that of boiling water. As soon as no further liquid condenses in the receiver, the colorless distillate, consisting of phosphorus oxychloride and methyl formyl chloride oxime, is well cooled and treated with an equal volume of water, to decompose the oxychloride. A colorless liquid is thus obtained, which, after standing over night in contact with calcium carbonate and calcium chloride, is found to distil without decomposition at 68° .

0.1300 gram substance gave 0.2005 gram AgCl (Carius).

0.1656 gram substance gave 21 cc. of moist N at $11^{\circ}.5$ and 760 mm. pressure.

	Calculated for C_2H_4ONCl .	Found.
Cl	37.90	38.16
N	14.98	15.12

Methyl formyl chloride oxime is a volatile liquid, slightly soluble in water. It possesses an odor strikingly similar to that of chloroform. In stability it closely resembles its homologue, benzyl formyl chloride oxime. It is unaffected by aniline at the ordinary temperature, but by prolonged heating at 100° , it is slowly acted upon with the separation of aniline hydrochloride. It is not attacked by silver nitrate, but is immediately decomposed when brought in contact with potassium or sodium hydroxides. If the powdered alkali be carefully added to well cooled methyl formyl chloride oxime, or better to its solution in dry ether or ligroin, an intense and unmistakable *isonitrile-like* odor is immediately produced. That this odor is due to the formation of minute quantities of methyl fulminate, $CH_3-O-N=C$, seems highly probable from the following considerations:

An ethereal solution of methyl formyl chloride oxime is completely freed from chlorine by treatment with an excess of powdered potassium hydroxide. If the solution be kept cool, the isonitrile odor is unaccompanied by any ammoniacal odor or reaction. On longer standing in contact with the potassium hydroxide, however, an amine odor arises and the vapor becomes alkaline in reaction.

An unsaturated body appears to result from the action of potassium hydroxide on methyl formyl chloride oxime. A ligroin solution, prepared as above, instantly decolorizes a small amount of bromine with the separation of minute yellow drops. The ligroin used, methyl formyl chloride oxime, and the methyl ester of formhydroxamic acid do not immediately decolorize a small amount of bromine.

To determine the nature of the odorous body, a solution of methyl formyl chloride oxime in absolute ether was treated with powdered potassium hydroxide and allowed to stand until action was completed. Little, if any, gas is evolved. After evaporating off the ether, a minute quantity of liquid, possessing a strong isonitrile odor, distilled over at from 50° to 60° (approximate temperature). The liquid remaining in the distilling-bulb and constituting the chief reaction-product, soon lost all odor of isonitrile. It was freed from traces of ether by warming and passing a current of air through it. A nitrogen determination seemed to indicate the presence of the methyl ester of formhydroxamic acid, $\text{CH}_3\text{—O—NH—CH=O}$.

0.1292 gram substance gave 20.7 cc. moist N at $14^{\circ}.5$ and 754.4 mm. pressure.

	Calculated for $\text{C}_2\text{H}_5\text{O}_2\text{N}$.	Found.
N	18.66	18.73

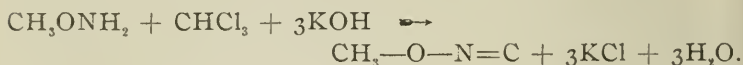
An attempt to distil the supposed ester under diminished pressure led to the isolation of only a very small quantity of substance, the contents of the distilling-bulb were largely converted into a resin.

The limited supply of material has thus far precluded a further study of this reaction; it is possible that the substance is a condensation-product of methyl fulminate.

Although, in the above experiment, it may be assumed that there is a direct interchange between the chlorine of the methyl formyl chloride oxime and the hydroxyl of the potassium hydroxide, it seems highly probable that the primary product of the reaction is the fulminic ester, $\text{CH}_3\text{—O—N=C}$. This, being in the nascent condition, may polymerize, or, by the ab-

sorption of a trace of water, be converted, in part, into the methyl ester of formhydroxamic acid. A minute quantity of the fulminic ester escapes further change and gives rise to the phenomena noted above.

A further indication of the presence of methyl fulminate in these reactions is that derived from the interaction of α -methyl hydroxylamine hydrochloride, chloroform, and alcoholic potassium hydroxide. With care, the same characteristic isonitrile odor noted above is obtained. It seems difficult to explain this on the basis of any other than the following reaction :



A continuation of the work will, it is hoped, lead to the definite isolation of the fulminic ester, or some of its addition-products.

UNIVERSITY OF CALIFORNIA,
BERKELEY, CAL.,
Aug. 23, 1904.

Contribution from the Kent Chemical Laboratory of the University of Chicago.
ON THE REACTIONS OF SODIUM BENZHYDROL.

BY RAYMOND FOSS BACON.

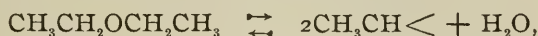
An exhaustive study by Nef¹ of benzhydrol and its derivatives, benzhydrol ether, bromdiphenyl methane, benzilic acid, etc., has shown that these substances possess very low dissociating-points. The dissociation-product common to all of them, diphenylmethylen, is not, however, capable of isolation as such. Similar results have been obtained by Miss Goldthwaite with the corresponding dibrom derivatives.² Since then it has been clearly proved by Nef³ that all primary and secondary alcohols undergo analogous dissociation into water and alkylidenes, the sole difference being in the fact that the decomposition-point varies within considerable limits, 300° to 600°. We have, as yet, no accurate means for determining the exact percentage of water and ethylidene particles present, for

¹ Ann. Chem. (Liebig), 298, 231-274.

² This JOURNAL, 30, 447.

³ Ann. Chem. (Liebig), 318, 138-230.

instance, in alcohol or ether at the ordinary temperature. As ether decomposes at a temperature which is 50° lower than the decomposition-point of alcohol, 600° , ether must obviously contain more dissociated particles,

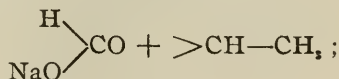
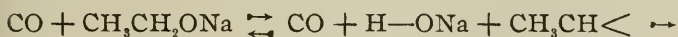


at the ordinary temperature than alcohol. This explains why ether burns slowly at ordinary temperatures, in the light, whereas this is not the case with alcohol, except in the presence of various catalytic agents, which have the effect of increasing most remarkably the percentage of the dissociated particles.

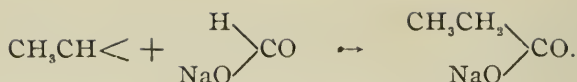
The experiments of Nef show further that if the hydroxyl hydrogen of an alcohol be replaced by a metal, such as Na, K, Ca, Ba, etc., the effect on the dissociating-point of the corresponding alcohol is most striking. The decomposition-point of sodium ethylate, for example, lies at 240° . Consequently there are, relatively, far more dissociated particles,



present at the ordinary temperature in sodium ethylate than in ether. Sodium ethylate, therefore, burns spontaneously, with considerable violence, in dry air or oxygen. The behavior of the metallic alcoholates of the aliphatic series has, in fact, been very thoroughly studied under the most varied conditions by Nef. He has found that they act as alkylating agents, and that they also decompose caustic alkalies with evolution of atomic hydrogen and can, therefore, act as reducing agents. Furthermore, it has been decisively established that the Geuther-Fröhlich reaction between carbonic oxide and sodium alcoholates is an alkylation phenomenon; *i. e.*, the reaction takes place in two stages, *viz.*, I.



and then only to a slight extent according to II.



In these experiments, therefore, the yield of alkylated formic acid is usually exceedingly small. It was found in one instance to be very large, namely, with 1,3-decyl alcohol.¹ On the other hand, the yield in the case of the alkylation of acetic acid with sodium alcoholates was invariably large—15 to 30 per cent. As the alkylidene can also necessarily interact with the caustic alkali—the other dissociation-product—with evolution of hydrogen and the formation of an aldehyde, ketone, or fatty acid, it is obvious that alkylation by means of sodium alcoholates can never take place quantitatively.²

A study of the salts of the aromatic alcohols, such as benzyl alcohol and benzhydrol, from the point of view developed by the work of Nef seemed especially desirable, and, consequently, work in this direction has been undertaken in this laboratory at Dr. Nef's suggestion, and under his guidance, by Mr. Higley and myself. I have confined my experiments chiefly to the benzhydrol series. As Mr. Higley's results in the benzyl series will presumably not be published for some time,³ I shall at times refer briefly to them where they have a bearing on my own work. A study of the dissociation phenomena in the benzhydrol series seemed of interest first, because Knoevenagel⁴ has recently, without sufficient basis, assumed a direct dissociation of benzhydrol into hydrogen and benzophenone, and secondly because it would be possible here to trace quantitatively all the reaction-products with great ease, as they must be crystalline, and their quantitative separation has already been worked out thoroughly by Nef (*loc. cit.*). The experiments performed with sodium benzhydrol were found to be entirely in harmony with the data obtained by Nef. It was possible to alkylate formic, acetic, and isobutyric acids by means of this salt. In the case of the acetic acid a 75 per cent yield

¹ Cf. Nef: *Ann. Chem. (Liebig)*, **318**, 150; Beatty: *This JOURNAL*, **30**, 224.

² *Ann. Chem. (Liebig)*, **318**, 148.

³ *This JOURNAL*, **30**, 225, foot-note.

⁴ *Ber. d. chem. Ges.*, **36**, 588.

of the monoalkylated acetic acid was actually obtained. These experiments finally led to an investigation of the action of sodium on benzyl acetate and allied compounds, and thus to a complete revision of the work Conrad and Hodgkinson¹ carried out in this direction some twenty-five years ago.

Preparation of Sodium Benzhydrol.—The benzhydrol used in all of my experiments was prepared according to the directions of Nef.² It was dissolved in 5 volumes of absolute ether, containing the calculated amount of sodium in the form of wire; the mixture was then heated under a reversed condenser until the metal had all disappeared. On cooling, sodium benzhydrol often crystallized out in large, transparent, colorless, crystalline plates, 2 to 3 cm. in length.

1.3830 grams substance, treated with water, required 65.1 cc. N/10 H₂SO₄ for neutralization.

1.0930 grams substance, treated with water, required 52.1 cc. N/10 H₂SO₄ for neutralization.

Na	Calculated for	Found.	
	(C ₆ H ₅) ₂ CHONa.		
	11.1	10.8	10.9

The salt quickly gains in weight in the air, owing to rapid absorption of water and oxygen; it turns green or greenish-blue in the light, and becomes colorless again over night. This phenomenon was noted for seven successive days, and reminds one of the behavior of benzhydrol ethyl ether described by Linnemann,³ although I have never noticed these phenomena in the latter case.

Dissociation of Sodium Benzhydrol.—The decomposition-point of this substance lies about 50° below that of benzhydrol, namely, at 250°. The salt, consequently, burns with considerable speed in dry air at the ordinary temperature. The products formed by heating the salt to the dissociating-point are benzene, sodium benzoate, and diphenyl methane, including, at times, also some tetraphenyl ethane and ethylene. Three

¹ Ann. Chem. (Liebig), **193**, 298; **201**, 166.

² *Ibid.*, **298**, 231-233.

³ *Ibid.*, **133**, 6.

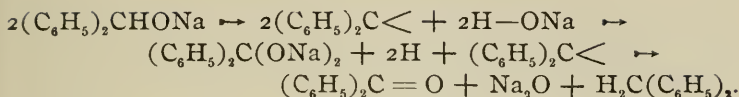
experiments were carried out quantitatively under slightly different conditions.

1. Twenty grams of sodium benzhydrol were heated in a distilling-flask for eight and a half hours in a metal bath, at a temperature ranging from 240° to 270° . The distilling-flask was connected with a condenser, a receiver, and an azotometer. The salt became at first bluish in color, but at the end was colorless again. No gaseous products were formed; the receiver contained 3.4 grams of liquid, from which, on fractionation, 2.9 grams of benzene, boiling from 75° to 80° , were obtained. The residue in the distilling-flask was worked up for neutral and acid products by extracting with dilute sodium hydroxide and ether. The ether extract gave, on crystallization from ligroin, 6.2 grams of benzhydrol, melting at 69° , and the filtrate gave 2.5 grams of diphenyl methane. Four and five-tenths grams of benzoic acid were obtained from the alkaline solution.

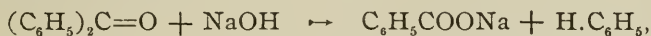
2. A second experiment, similar to 1, and using the same amount of material, but heating during four hours at 260° to 290° , and for a short time to 300° , showed some blackening and gas evolution (only at 300°). The reaction-products were found to be 3.1 grams of benzene, 4.2 grams of benzoic acid, 7.7 grams of diphenyl methane, 0.5 gram of tetraphenylethylene, 0.4 gram of tetraphenyl ethane, and 1.1 grams of benzhydrol.

Benzophenone was not present in either 1 or 2, as was proved by digestion of the neutral product with alcoholic phenylhydrazine, after removal of the benzhydrol with cold ligroin.

3. Twenty grams of sodium benzhydrol were heated in a sealed tube at 270° to 280° for forty hours (five successive days of eight hours each). No pressure was observed on opening the tube. The residue had a yellowish tinge, and was somewhat blackened in the middle. The reaction-products were determined as 2.6 grams of benzene, 5.5 grams of benzoic acid, 7.3 grams of diphenyl methane, and 3.1 grams of benzhydrol. Therefore, the following main reaction takes place on heating sodium benzhydrol to its decomposition-point :



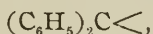
The reaction is obviously entirely analogous to the one which takes place between benzaldehyde and potassium hydroxide at the ordinary temperature.¹ That under the conditions of the experiment the benzophenone first formed must be rapidly and completely converted into equal amounts of benzene and sodium benzoate,



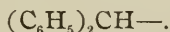
follows from the observations of Chancel² on benzophenone, and was also established by special experiment.

An intimate mixture of 10 grams of benzophenone and 2.2 grams of sodium hydroxide were heated for one hour at 260° to 270° (apparatus as in 1, above) ; 3.6 grams of benzene, boiling from 78° to 80°, were obtained from the distillate in the receiver ; the residue in the distilling-flask gave 4.5 grams of benzoic acid.

The small amount of tetraphenylethylene and ethane observed in Experiment 2, above, is probably due to a polymerization of the nascent molecules of diphenyl methylene,

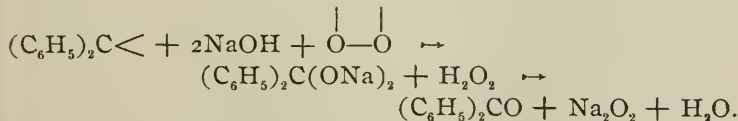


and diphenyl methyl,



The Spontaneous Combustion of Sodium Benzhydrol in Dry Air.

—According to Nef's interpretation of combustion phenomena,³ the following reaction between the dissociated sodium benzhydrol molecules and the active oxygen molecules of the air must take place at considerable speed on passing dry air and oxygen over sodium benzhydrol at the ordinary temperature :

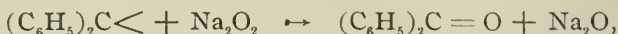


¹ Nef : Ann. Chem. (Liebig), 298, 301-302.

² *Ibid.*, 72, 280.

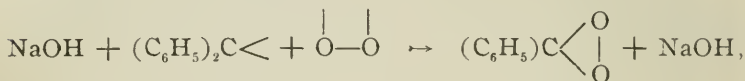
³ *Ibid.*, 298, 294-301, 322-332 ; 318, 177-182.

This was found to be the case. The sodium peroxide is, however, in great part used up in oxidizing the unchanged diphenylmethyle particles,



so that only 21.67 per cent of the sodium peroxide was actually isolated, as such, at the end of the experiment. No trace of a per-

oxide, $(\text{C}_6\text{H}_5)_2\text{C} \begin{smallmatrix} \diagup \text{O} \\ | \\ \diagdown \text{O} \end{smallmatrix}$, such as would be demanded by Engler and Bach's interpretation of combustion phenomena,



was found in my oxidation experiments. Nef also failed to obtain a trace of the stable acetone peroxide of Baeyer in his experiments on the oxidation of sodium isopropylate.¹

1. Twenty-five grams of sodium benzhydrol were placed in a large flask and a stream of air, dried by a combustion train, was slowly passed over it. A perceptible rise of temperature was observed after an hour and the gain in weight, after nine hours, was 1 gram. The mass had now a greenish tint and appeared moist. Dry oxygen was then passed over the mixture for ten hours, with no apparent change. The mass was directly extracted with absolute ether; no benzene was present, and the ether extract gave, on fractionation under 25 mm., 16.2 grams of perfectly pure benzophenon ebolling at 180° to 182°. It solidified immediately on addition of a crystal of benzophenone, and then all melted at 47°. A portion, 5 grams, gave, on digestion with 3.7 grams of phenylhydrazine and an equal weight of alcohol, 7 grams of benzophenone phenylhydrazone melting at 137° (theory 7.47 grams). The portion insoluble in ether, 7 grams, was treated with water and extracted with ether. The alkaline solution gave a marked test for carbonic acid, and, on acidifying, 0.8 gram of benzoic acid, melting at 121°, was obtained. The solution also gave a most pronounced test for hydrogen peroxide with

¹ Ann. Chem. (Liebig), 318, 181.

bichromate and ether. On treatment of a portion of the solution with benzoyl chloride, according to v. Pechmann,¹ a precipitate of dibenzoyl peroxide, melting at 104°, was obtained.

2. In order to determine the amount of hydrogen peroxide quantitatively, a fresh oxidation experiment was carried out with 10 grams of sodium benzhydrol. During the oxidation (air eight hours, oxygen forty-four hours) the distilling-flask containing the salt was kept immersed in ice-water. The reaction-products were at once treated with water and an excess of potassium iodide added. The amount of iodine set free was then determined by means of sodium thiosulphate (preliminary experiments having shown that this method was accurate for the work in hand) ; 0.39 gram of sodium peroxide, or 21.67 per cent of the amount demanded by the above theory, was found.

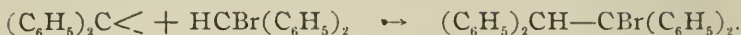
On the Combustion or Oxidation of Bromdiphenylmethane.—The experiments of Nef have proved that not only primary and secondary alcohols, their salts, and ethers, but also the primary and secondary alkyl haloids, the aldehydes, ketones, fatty acids, substituted ammonias, paraffines, etc., undergo methylene dissociation. Ethane, toluene, diphenyl methane, when first oxidized, give acetaldehyde, benzaldehyde and benzophenone, respectively, because these substances are partially dissociated at the ordinary temperature, *e. g.*,



It was, therefore, of interest to try the action of oxidizing agents on bromdiphenyl methane. This substance possesses, as Nef has shown, a low dissociation-point, 250°. It ought, therefore, to oxidize slowly in dry air, at the ordinary temperature, to benzophenone. Miss Goldthwaite has, indeed, shown that such an oxidation takes place with the analogous paradibromdiphenyl methyl bromide. When, however, either of these compounds is heated to the decomposition-point, 250°, without air access, hydrogen bromide is eliminated quantitatively, but the diphenyl methylene residues first set free either polymerize directly to the dimolecular derivatives, or give

¹ Ber. d. chem. Ges., 27, 1511.

these end-products by an intermediate alkylation and subsequent loss of hydrogen bromide,



That the dissociation of these compounds is monomolecular and not bimolecular is furthermore proved by the fact that, when the heating is carried out in a stream of dry air or oxygen, benzophenone and paradibrombenzophenone, respectively, are formed quantitatively. This proves that the diphenyl methylene residues first set free combine preferably with the oxygen to give the corresponding oxides. The reaction is, therefore, perfectly analogous to the combustion of sodium benzhydrol presented above. In the light of what has just been said, the results of the following experiments with bromdiphenyl methane are self-evident :

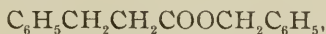
1. Ten grams of bromdiphenyl methane were treated in the cold, and in a solution acidified with sulphuric acid, with aqueous potassium permanganate until no further decolorization took place. The solution was extracted with ether and the oil obtained was then digested with phenylhydrazine and alcohol. Nine and one-tenths grams of benzophenone phenylhydrazone, melting at 136° , were obtained.

2. Five grams of bromdiphenylmethane were placed in a distilling-flask connected with a reversed condenser and dry oxygen steadily passed through the molten substance, which was heated in a metal-bath at 160° to 170° . Streams of hydrogen bromide came off at first, and practically ceased after three and one half hours' heating. The oil left in the distilling-flask boiled chiefly at 160° to 170° under 10 mm. pressure, and gave, on digestion with phenylhydrazine and alcohol, 5.3 grams of benzophenone phenyl hydrazone melting at 137° . Nine-tenths gram of the tetraphenyl ethylene, melting at 218° , were found in the distilling-flask after the removal of the benzophenone by distillation.

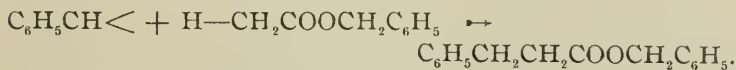
3. Five grams of bromdiphenyl methane, dissolved in absolute ether, were left standing in the cold for two weeks with 3 grams of sodium in the form of wire. One and two-tenths

grams of tetraphenyl ethane and 1.1 grams of diphenyl methane were obtained as reaction-products.

The Action of Sodium Benzhydrol on Benzhydrol Acetate.—As is well known through the work of Geuther, Claisen and others, esters of acetic acid are converted into acetoacetic ether by treatment with sodium or sodium alcoholates. The reaction has been shown by Nef to belong to the category of olefine condensations, and is therefore reversible. In connection with the earlier experiments on the esters of acetic acid, it was found that esters containing an aliphatic group, such as methyl, propyl, and isoamyl acetate, all give a fair yield of the corresponding acetoacetic ester, on treatment with sodium or with sodium alcoholates. On trying the experiment with benzyl acetate and sodium, however, Conrad and Hodgkinson found, to their great surprise, that no trace of acetoacetic benzyl ester was obtained.¹ An interaction between the reagents took place at 135° and then proceeded with some violence. According to their investigations, benzyl hydrocinnamate,



is the chief reaction-product. Such a result could now be readily understood in view of the experiments of Nef on the alkylation of the fatty acids by means of sodium alcoholates. The phenyl methylene particles, resulting from the dissociation of the sodium benzylate first formed, must alkylate the unchanged benzyl acetate as follows:²

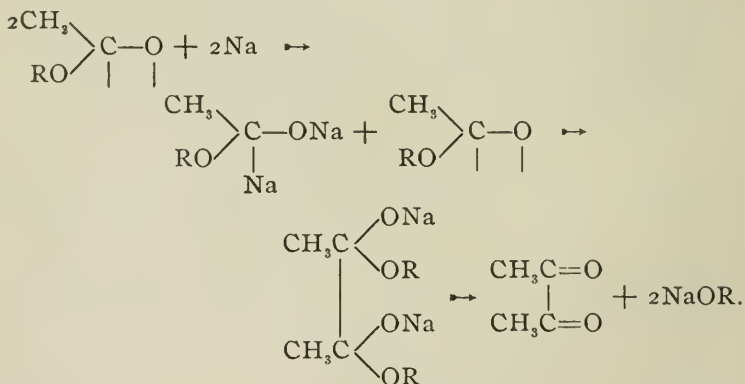


A more careful investigation of the reaction of Conrad and Hodgkinson, which is described in detail below, has proved that much benzyl ether is formed besides benzyl hydrocinnamate. The question now arises, why do not benzyl acetate and sodium interact to give an ester of acetoacetic acid? The same question presents itself in the case of benzhydrol acetate. The problem was first taken up in this laboratory by Shaklee,

¹ Ann. Chem. (Liebig), 193, 298.

² Ibid., 318, 144; Cf. This JOURNAL, 30, 225, foot-note.

who proved that benzyl acetate and benzhydropyruvate readily react with sodium in absolute ethereal solution in the cold. He found that very little hydrogen was given off in the course of the reaction, and that the chief products were acetic acid, and benzyl alcohol, or benzhydropyruvate, respectively. In both cases, however, the formation of a small amount of diacetyl was observed. Shaklee established this rigidly by the isolation of the osazone, which was analyzed and found to be identical in its properties with the statements given in the literature. This result, in conjunction with the other facts observed, proves that some esters of acetic acid can react with sodium in a manner entirely different from ethyl acetate. The experiments of Nef on the action of sodium on carbonyl compounds¹ make it exceedingly probable that the following reaction between sodium and acid esters can take place :



No hydrogen is formed in this reaction and the yield of diacetyl must necessarily remain low, because all orthodicarbonyl compounds undergo a benzilic acid rearrangement, *i. e.*, a conversion into glycollic acid derivatives, especially in the presence of strong alkali. It is, therefore, quite probable that dimethylglycollic acid was formed in Shaklee's experiments but was overlooked by him.

The fact that ethyl isobutyrate gives diisopropylglycollic acid derivatives as the chief reaction-products² on treatment

¹ Ann. Chem. (Liebig), 308, 283, 292; Cf. Acree : This JOURNAL, 29, 588.

² Hantzsch : Ber. d. chem. Ges., 20, 2332; Ann. Chem. (Liebig), 249, 54; 246, 129.

with sodium, in absolute ethereal solution, taken in connection with Shaklee's isolation of diacetyl, makes this assumption almost a certainty. These results at once bring up the question whether ethyl acetate itself may, to some extent, not react in an analogous manner with metallic sodium. The amount of hydrogen actually evolved in the manufacture of acetoacetic ether from acetic ether and sodium is only 36.5 per cent of the theoretical amount in the most favorable case.¹ The preliminary experiments which I have carried out in this direction are very striking, and seem to justify these conclusions. When ethyl acetate, carefully dried, is diluted with 10 parts of absolute ether and treated with one atomic proportion of sodium, the metal disappeared entirely after twenty-four hours' standing. Only traces of acetoacetic ether and of hydrogen were obtained under these conditions, although the experiment was tried five times, using 176 grams of ethyl acetate in each experiment. It is the intention of Dr. Nef to investigate this reaction in the near future with the greatest of care. The results obtained show, however, that the recent assumption of Michael² that ethyl acetate first gives the salt $\text{CH}_2\text{NaCOOC}_2\text{H}_5$, etc., on treatment with sodium cannot possibly be correct. Experiments in this connection by Higley have further proved that a mixture of 2 molecules of ethyl acetate and 1 molecule of sodium ethylate, on standing for a week at ordinary temperatures, gives a 26.7 per cent yield of acetoacetic ester; on standing for twenty-five days a 36.1 per cent yield of the ester was obtained.³

In order to determine why the corresponding condensation between sodium benzyolate and benzyl acetate, as well as between sodium benzhydrol and benzhydrol acetate does not take place to any extent, it was obviously first necessary to prepare benzyl- and benzhydrolacetoacetate and study their properties.

Benzyl Acetoacetate, $\text{CH}_3\text{COH} : \text{CHCOOCH}_2\text{C}_6\text{H}_5$.—This ester has been prepared and analyzed by Shaklee, who obtained it, almost quantitatively, by heating a mixture of 20 grams of

¹ Cf. Meyer : J. prakt. Chem., [2], **65**, 528.

² Ber. d. chem. Ges., **33**, 3731.

³ Cf. E. V. Meyer : J. prakt. Chem., [2], **65**, 528.

benzyl alcohol and 40 grams of acetoacetic ethyl ester in a distilling-flask connected with a condenser and Brühl apparatus. The bath was kept at 160° and as soon as no more ethyl alcohol distilled over, the apparatus was exhausted. Thirty-four grams of benzyl acetoacetate, boiling at 162° to 164° under 16 mm. pressure, was obtained as a colorless mobile oil, smelling like ordinary acetoacetic ester. The oil boils, with some decomposition, at about 270° , gives a blood-red coloration with alcoholic ferric chloride, is insoluble in alkali carbonates, but dissolves without decomposition in cold aqueous sodium hydroxide.

The copper salt, which has been analyzed by Higley, is precipitated quantitatively by means of aqueous alcoholic copper acetate. It crystallizes well from benzene, and melts at 156° . Experiments by Shaklee and Higley have shown that benzyl-acetoacetate is never formed in amounts greater than 2 per cent on treatment of benzyl acetate with sodium or with sodium benzyolate under the most varying conditions (20° , 100° , 140°). Higley's experiments prove, furthermore, that benzyl acetoacetate is readily decomposed by heating it with sodium benzyolate at 100° or at a still higher temperature. Consequently only traces of benzyl acetoacetate are obtained from mixtures of benzyl acetate and sodium or sodium benzyolate when heated above 100° . These data, therefore, prove that benzyl acetoacetate is formed from its components by the aldol condensation, but in relatively far smaller amounts than ethylacetoacetate. The great difference in the yield, as the reaction is reversible, is simply due to the far greater relative instability of benzyl acetoacetate. My own experiments in the benzhydrol series confirm in every way these observations of Higley.

Benzhydrol Acetoacetate, $\text{CH}_3\text{COH}:\text{CHCOOCH}(\text{C}_6\text{H}_5)_2$.—Fifty grams of benzhydrol dissolve in 100 grams of ordinary acetoacetic ether with marked lowering of temperature (23° to 10°). This mixture was heated in an oil-bath at 150° for one hour; much ethyl alcohol distilled over. The oil left in the distilling-flask was now heated *in vacuo* at 200° , the non-volatile portion dissolved in cold sodium hydroxide, and the neutral constituents extracted with ether. The alkaline solution gave,

on acidifying with sulphuric acid and extracting with ether, 51 grams of crude oil, which soon solidified. By crystallizing from ether-ligroin, benzhydrol acetoacetate was obtained in colorless plates, melting at 56° . The substance is very soluble in the ordinary organic solvents except ligroin. It smells like acetoacetic ether and gives a deep purple coloration with ferric chloride. It is insoluble in alkali carbonates and, like all benzhydrol derivatives, gives a deep red coloration with concentrated sulphuric acid.

0.2291 gram substance gave 0.6329 gram CO_2 and 0.1228 gram H_2O .

	Calculated for $\text{CH}_3\text{COH} : \text{CHCOOCH}(\text{C}_6\text{H}_5)_2$.	Found.
C	76.1	75.4
H	6.0	6.0

The copper salt is precipitated quantitatively by means of aqueous alcoholic copper acetate. It crystallizes from benzene as a powder, melting at 174° to 176° . The following experiments show that, at best, it is possible to obtain benzhydrol acetoacetate only in very small amounts from mixtures of benzhydrol acetate and sodium benzhydrol; this is due, in part or entirely, to the great instability of sodium benzhydrol acetoacetate under these conditions. It may, however, also be due in part to the greater stability of the orthoacetic acid addition-

product, $\text{CH}_3\text{C} \begin{array}{l} \nearrow \text{OCH}(\text{C}_6\text{H}_5)_2 \\ \text{---} \text{OCH}(\text{C}_6\text{H}_5)_2 \\ \searrow \text{ONa} \end{array}$, which must necessarily be first

formed on mixing these reagents.¹

1. Twenty-two and six-tenths grams of benzhydrol acetate (2 mols.) and 10.3 grams of sodium benzhydrol were intimately mixed. There is a noticeable heat evolution, owing to the formation of the ortho addition-product. The mixture was heated in a sealed tube at 100° for fifteen hours. The mass was then treated with dilute sulphuric acid and worked up as usual for products soluble in sodium hydroxide and sodium carbonate. A small amount of β -diphenylpropionic acid, the monoalkylated acetic acid (see below), was obtained, besides

¹ Claisen : Ber. d. chem. Ges., 20, 648.

acetic acid. The sodium hydroxide solution gave 0.4 gram of benzhydrol acetoacetate, melting at 53° , and identical in its properties with the ester described above. The neutral portion gave 14 grams of benzhydrol, which melted at 68° and crystallized from ligroin. Ten grams of oil, boiling at 176° to 183° under 17 mm. pressure, were also obtained. This was proved to be free from benzophenone by digestion with alcoholic phenylhydrazine. On saponification with alcoholic potash the oil gave 7.8 grams of benzhydrol, hence it consisted of benzhydrol acetate.

2. Five grams of benzhydrol acetoacetate and 8 grams of sodium benzhydrol (2 mols.), treated as in 1, gave 6 grams of benzhydrol and small amounts of benzophenone; the latter was probably formed through a spontaneous oxidation of sodium benzhydrol, as the mixture stood in the air before being worked up. No unchanged benzhydrol acetoacetate was found.

3. Twenty-two and six-tenths grams benzhydrol acetate (4 mols.) and 5.1 grams of sodium benzhydrol, treated as in 1, gave only traces of β -diphenylpropionic acid, 8.5 grams of benzhydrol, and 14.7 grams of unchanged benzhydrol acetate.

4. Ten grams of benzhydrol acetate, dissolved in absolute ether and treated with 7 grams of sodium in the form of wire, reacted completely in the cold. On working up as in 1, 4 grams of benzhydrol and only traces of benzhydrol acetoacetate were obtained. It is to be emphasized that Shaklee obtained also small amounts of diacetyl under similar conditions.

The experiments, 1 to 4, show that mixtures of benzhydrol acetate and sodium benzhydrol or sodium do not interact to give an appreciable amount of benzhydrol acetoacetate. It was now of interest to determine what would happen if molecular amounts of these reagents were heated to a higher temperature (150° to 300°). It is obvious from the experiments of Nef that the dissociated molecules coming first from the sodium benzhydrol, and also from the dissociated benzhydrol acetate (see below), might alkylate the benzhydrol acetate or the sodium acetate,



which would result in the formation of β -diphenylpropionate or its benzhydrol ester. The experiment was therefore tried, and, under the most favorable conditions (300°), a yield of 75 per cent of the theoretical amount of β -diphenylpropionic acid was actually obtained.

Benzhydrol β -Diphenylpropionate,

$(\text{C}_6\text{H}_5)_2\text{CHCH}_2\text{COOCH}(\text{C}_6\text{H}_5)_2$. — As this ester might be formed by direct alkylation of benzhydrol acetate it was synthesized and studied. On account of the very stable properties ascribed by Conrad and Hodgkinson (*loc. cit.*) to the analogous benzyl hydrocinnamate, it was at first expected that the ester must be exceedingly difficult to saponify. This was found, however, not to be the case, and later experiments (see below) with the real synthetic benzyl hydrocinnamate have proved that it also can be saponified with the greatest of ease by means of alcoholic potassium hydroxide in the cold.

β -Diphenylpropionic acid was prepared according to the directions of Henderson.¹ The melting-point of the acid, after crystallization from ligroin, was found to be 155° , whereas Henderson gives 151° . The acid crystallizes in needles and gives no coloration on standing with concentrated sulphuric acid. It is not volatile with steam. Heated with an equal weight of sodium benzhydrol for six hours, in a sealed tube, at 300° to 310° , it was recovered entirely unchanged. The potassium salt of β -diphenylpropionic acid, dissolved in an equal weight of the free acid, was now heated with the theoretical amount of bromdiphenylmethane for five hours at 150° to 160° . The neutral product thus obtained, which was insoluble in cold ether and soluble in cold benzene, was recrystallized from alcohol and colorless needles, melting at 112° , were obtained. The ester is difficultly soluble in ether and cold alcohol, but very soluble in benzene.

0.1831 gram substance gave 0.5747 gram CO_2 and 0.1072 gram H_2O .

¹ J. Chem. Soc. (London), 59, 734.

	Calculated for (C ₆ H ₅) ₂ CHCH ₂ COOCH(C ₆ H ₅) ₂ .	Found.
C	85.7	85.4
H	6.1	6.2

Benzhydrol β -diphenylpropionate was saponified with the greatest ease by heating 5 grams in an oil-bath at 110°, for one hour, with 1.25 mol. potassium hydroxide in 10 grams alcohol. Two grams of benzhydrol and 2.5 grams of β -diphenylpropionic acid (theory 2.8 grams), melting at 154°, were obtained as reaction-products.

On the Alkylation of Acetic Acid by Sodium Benzhydrol.—This was accomplished in a variety of ways, all of which depend on the same principle, namely, the absorption of an acetate by diphenylmethylen coming from the dissociation of a benzhydrol salt. The following experiments need, therefore, no further elucidation :

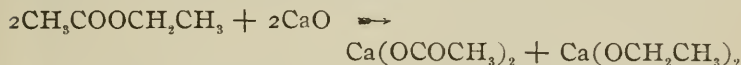
1. Ten grams of ethyl acetanilide and 12 grams of sodium benzhydrol were carefully mixed in a sealed tube until homogeneous, and were then heated for eight hours at 160° to 170°, and finally for three hours at 220°. The reaction-products were found to be as follows : 6.5 grams of ethyl aniline, 6.1 grams of benzhydrol, 1.1 grams of benzhydrol ether, traces of tetraphenyl ethane, and a small amount of benzophenone (identified as phenylhydrazone, 1.7 grams melting at 136°, being obtained). The solid acid product was found to consist only of β -diphenylpropionic acid (1.1 grams melting at 155°).

2. A second experiment, using 10 grams of ethyl acetanilide and 15 grams sodium benzhydrol, gave, after heating in a sealed tube for fifty hours (in periods of about eight hours daily), 6.5 grams of ethyl aniline, 5.2 grams benzhydrol, 1.5 grams of β -diphenylpropionic acid, 1.4 grams of tetraphenylethane, and a small amount of benzophenone (1.2 grams of phenylhydrazone being isolated).

3. 25 grams of benzhydrol acetate and 7 grams of quicklime were intimately mixed and heated in a sealed tube for six hours at 230° to 250°. Four-tenths gram of β -diphenylpropionic acid, 7.5 grams of tetraphenylethane, 6 grams of benzhydrol ether, 3.2 grams of benzhydrol, besides a small amount

of benzophenone (4.1 grams phenylhydrazone) were obtained as reaction-products.

This experiment is of interest in connection with the formation of *n*-butyric acid, observed by Ljubawin,¹ on heating ethyl acetate with quicklime at 250° to 280°. Calcium ethylate and acetate are obviously first formed,



the ethylidene, resulting from the dissociation of calcium ethylate, alkylates the acetate, giving calcium butyrate.

4. An intimate mixture of 16 grams benzhydrol acetate and 20 grams of sodium benzhydrol was heated for thirty hours, in a sealed tube, at 150° to 160°. There was no pressure on opening the tube, and 1.5 grams β -diphenylpropionic acid, besides 3.1 grams of benzhydrol β -diphenylpropionate were obtained. The other products were 19 grams benzhydrol, 1.5 grams benzhydrol ether, 1 gram tetraphenylethylene, traces of tetraphenylethane and a small amount of benzophenone.

5. Twelve grams of benzhydrol acetate and one atomic proportion of sodium (1.2 grams) were heated under a reversed condenser. There was no action at 100°; as soon as the bath reached 130° to 140° the metal dissolved rapidly and, after an hour's heating at that temperature, the following products were obtained: 1.1 grams β -diphenylpropionic acid, 6.5 grams of benzhydrol, 0.5 gram tetraphenylethylene, besides traces of the corresponding ethane derivative, and benzophenone (3.1 grams phenylhydrazone).

It will be noticed that the yield of monoalkylated acetic acid obtained in experiments 1 to 5 is not very large. At first this was attributed to a decomposition of this acid because Nef has shown that the fatty acids have comparatively low dissociation points.² Furthermore, the fact observed by Karsten³ that β -diphenylpropionic acid gives benzophenone by oxidation with potassium permanganate points to a possible dissociation

¹ Jour. Russ. Chem. Ges., **12**, 81.

² Ann. Chem. (Liebig), **318**, 220.

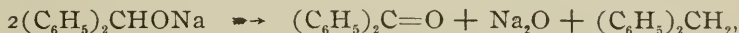
³ Ber. d. chem. Ges., **26**, 1579.

yield of alkylated fatty acid is increased by an addition of benzophenone :

1. An intimate mixture of 10 grams of benzhydrol acetate, 10 grams of sodium benzhydrol and 5 grams benzophenone was heated in a sealed tube for six hours at 300°. Three and nine-tenths grams of β -diphenylpropionic acid, 3.5 grams diphenylmethane, 3.8 grams of benzhydrol and benzophenone (9 grams of phenylhydrazone) were obtained.

2. An intimate mixture of 10 grams benzhydrol acetate and 10 grams of sodium benzhydrol was heated in a sealed tube at the same time and in the same furnace as used in 1. The products formed were 3.4 grams β -diphenylpropionic acid, 3.4 grams benzhydrol, 4 grams diphenylmethane, and benzophenone (4.5 grams phenylhydrazone).

These experiments show very clearly that a considerable portion of the sodium benzhydrol decomposes as such (see above),



giving benzophenone and diphenylmethane, and these are found mostly unchanged at the end of the experiment. This explains why it is necessary to use more than 1 molecular proportion of sodium benzhydrol in order to obtain a very large yield of β -diphenylpropionic acid (see above experiment with 2 molecular proportions of alcoholate at 300° to 310°). The slightly larger yield of monoalkylated acetic acid obtained in experiment 1, as compared with experiment 2, is easily understood because a portion of the benzophenone added must necessarily be reduced to benzhydrol¹ by the atomic hydrogen set free by the action of diphenylmethylene on sodium hydroxide. For that reason also the amount of diphenylmethane obtained in 1 is proportionally less than that found in 2.

The reactions under consideration therefore unquestionably belong to the category of alkylation phenomena. That the acetyl radical is alkylated directly by the diphenylmethylene particles, and not indirectly through an intermediate acetoacetic ether formation, is in the highest degree probable from

¹ Cf. Nef : Ann. Chem. (Liebig), 318, 183.

the data presented above on the benzyl and benzhydrol acetoacetate.

There are, however, undoubtedly some cases where the alkylation depends partially or entirely on an intermediate formation of acetoacetic acid derivatives, and other cases where it is impossible to decide decisively between these two possibilities—which necessarily, however, lead to the same end result.

Furthermore, there is no doubt that the hydrogen atom in formic acid derivatives, $X-C \begin{smallmatrix} \nearrow O \\ \searrow H \end{smallmatrix}$, and the tertiary hydrogen

atom in isobutyric acid derivatives, $X-CO-C \begin{smallmatrix} \nearrow (CH_3)_2 \\ \searrow H \end{smallmatrix}$, is capable of direct alkylation by diphenylmethylene, as is shown by the following experiments :

Alkylation of Benzhydrol Formate.—Benzhydrol formate is readily obtained by heating a solution of 20 grams of potassium formate and 50 grams of bromdiphenylmethane, in formic acid, in a sealed tube, at 100° , for about ten hours. The benzhydrol formate was obtained as a neutral, colorless oil, boiling at 159° to 160° under 10 mm. pressure. An intimate mixture of 10 grams of this oil with 12 grams of sodium benzhydrol was heated in a sealed tube for eight hours, at 300° to 310° , and on working up for acids 0.2 gram pure diphenyl acetic acid, melting at 146° , were obtained ; it was recrystallized from water and ligroin and coincided in its properties with those given in the literature.¹ It is quite probable that a much larger yield could be obtained by further work.

Benzhydrol Isobutyrate, $(CH_3)_2CHCOOCH(C_6H_5)_2$.—A mixture of 50 grams bromdiphenylmethane, 30 grams potassium isobutyrate, and 50 grams isobutyric acid was heated under a reversed condenser for one hour at 150° ; on pouring into water, extracting with ether, washing with sodium hydroxide, and drying the ethereal solution with calcium chloride, 58 grams of benzhydrolisobutyrate, boiling at 185° to 187° under

¹ Klingemann : Ann. Chem. (Liebig), **275**, 84 ; Zincke : *Ibid.*, **171**, 122 ; Dunlap : This JOURNAL, **19**, 645.

15 mm. pressure, were obtained. The oil soon changed to a colorless solid which melted at 54° , is quite soluble in cold alcohol and ether, and can be crystallized from low-boiling ligroin.

0.1912 gram substance gave 0.5623 gram CO_2 and 0.1239 gram H_2O .

	Calculated for $(\text{CH}_3)_2\text{CHCOOCH}(\text{C}_6\text{H}_5)_2$.	Found.
C	80.3	80.2
H	7.1	7.2

Alkylation of Benzhydrolisobutyrate, 1-Dimethyl-2-diphenylpropionic Acid, $(\text{C}_6\text{H}_5)_2\text{CHC}(\text{CH}_3)_2\text{COOH}$.—Nef's experiments with sodium isobutyrate and benzophenone at 190° to 220° have already proved that isobutyric acid is capable of alkylation by diphenylmethylenes, and the following experiments simply confirm his results:¹

1. An intimate mixture of 15 grams of benzyl isobutyrate and 25 grams of sodium benzhydrol was heated in a sealed tube, for five hours, at 190° to 220° . The following products were obtained: 0.8 gram of 1-dimethyl-2-diphenylpropionic acid, in plates, from ligroin, melting at 134° ; 22 grams of benzhydrol; 4 grams of diphenylmethane; and benzophenone (4 grams of phenylhydrazone).

2. Twenty-two grams benzhydrol isobutyrate and 15 grams of sodium benzhydrol were heated in a sealed tube, for twenty-six hours, at 100° . Three grams of isobutyric acid and 0.3 gram of monoalkylated isobutyric acid were obtained, besides 16 grams of benzhydrol, 3 grams of diphenylmethane, and 10 grams of unchanged benzhydrol isobutyrate.

3. Fifteen grams each of benzhydrol isobutyrate and sodium benzhydrol were heated in a sealed tube for two and one-half hours, at 270° to 275° . There was some pressure on opening the tube. One-tenth gram benzoic acid and 2.7 grams of 1-dimethyl-2-diphenylpropionic acid (separated by distillation with steam) were obtained. The neutral products were 6 grams of benzhydrol, 4.7 grams of diphenylmethane, and benzophenone (2.4 grams phenylhydrazone).

¹ Ann. Chem. (Liebig), 318, 184.

4. Ten grams of benzhydrol isobutyrate and 20 grams of sodium benzhydrol were heated in a sealed tube, for twenty hours, at 200° to 220° . Only 0.8 gram of monoalkylated isobutyric acid was obtained. The other products were 22 grams benzhydrol, 3 grams diphenylmethane, and benzophenone (5.9 grams phenylhydrazone).

5. Ten grams of benzhydrol isobutyrate and 15 grams sodium benzhydrol were heated in a sealed tube, for eight hours, at 300° to 310° . Four grams of benzoic acid and 3.1 grams monoalkylated isobutyric acid were obtained. The neutral portion gave 6.1 grams of diphenylmethane, and benzophenone (5.9 grams phenylhydrazone).

6. Ten grams benzhydrol isobutyrate and 20 grams sodium benzhydrol heated in a sealed tube, for eight hours, at 270° to 300° , gave 6.3 grams of benzoic acid and 2.8 grams of 1-dimethyl-2-diphenylpropionic acid, 8.2 grams diphenylmethane, 1.2 grams benzhydrol and benzophenone (3.6 grams phenylhydrazone) were obtained from the neutral portion.

The experiments 1 to 6 show that, at best, the yield of monoalkylated isobutyric acid is about 30 per cent; the sodium benzhydrol, in great part, decomposes, as such, by heating, and therefore about equal molecules of diphenylmethane and benzophenone (or its decomposition-products) are always obtained.

The Dissociation of Benzhydrol Acetate.—Nef's experiments have proved that benzhydrol and its derivatives, such as benzhydrol ether, benzhydrol ethyl ether, benzhydrol acetate, benzoate, etc., all dissociate at 300° into diphenylmethylene.¹ This explains why, with concentrated sulphuric acid, all these compounds, as well as benzilic acid, give the same deep red coloration which is simply due to the formation of polymerized diphenylmethylene particles. Preliminary experiments by Nef with benzhydrol acetate² have shown that this substance decomposes at 300° , giving acetic acid, tetraphenylethylene, and ethane. I have studied this reaction more in detail, with larger amounts of material. Twenty-five grams of benzhydrol acetate were heated in a sealed tube, at 300° to 310° , for

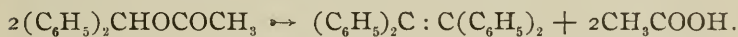
¹ Ann. Chem. (Liebig), 298, 231-245.

² Loc. cit., p. 244.

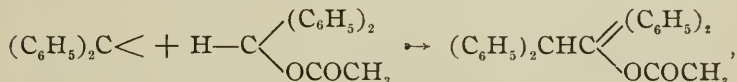
twenty-four hours, *i. e.*, for three days of eight hours each. No pressure was noticed on opening the tube, but the contents were dark-colored and gave a strong odor of acetic acid.

On adding sodium hydroxide and ether a portion remained insoluble and was filtered off and dissolved in cold benzene. Tetraphenylethane must, therefore, be absent. The benzene extract gave, on addition of alcohol, 10.8 grams of pure tetraphenylethylene, melting at 221° . Not a trace of β -diphenylpropionic acid (monoalkylated acetic acid) could be found in the alkaline solution. The ether extract gave, on fractionation under 10 mm. pressure, 4.9 grams of oil boiling at 140° to 170° . This, on treatment with alcoholic phenylhydrazine, yields 2.5 grams of benzophenone phenylhydrazone, melting at 137° , and 2.1 grams of diphenylmethane boiling at 255° to 260° .

The experiment just described shows that 60 per cent of the benzhydrol acetate decomposes as follows :

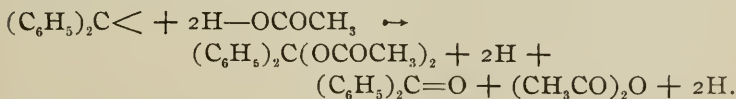


The formation of tetraphenylethylene may be due to a direct polymerization of the diphenylmethylene particles as such, or is more probably due to an alkylation of the non-dissociated benzhydrol acetate by the diphenylmethylene,¹



with subsequent loss of acetic acid from the addition-product thus formed.

A portion of the diphenylmethylene particles probably also act with the acetic acid as follows :



The atomic hydrogen thus set free is at once absorbed by more diphenylmethylene to give diphenylmethane. This explains, in an adequate manner, the formation of benzophenone and

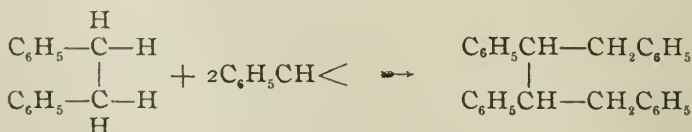
¹ Cf. Nef: *Ann. Chem.* (Liebig), **335**, 261.

diphenylmethane in the dissociation experiment with benzhydrol acetate described above.

Nef has repeatedly called attention to the fact that catalytic agents increase, to a very marked extent, the percentage of dissociated particles present at a definite temperature. The following experiment is of interest in this connection: On May 1st, 1903, I placed in the sunlight a sealed tube containing 10 grams of molten benzhydrol acetate. The liquid soon assumed a yellow color with greenish tinge. The tube stood until Oct. 19th, of the same year, and by that time a considerable amount of solid had separated. A strong odor of acetic acid was noticed on opening the tube; 1.7 grams of tetraphenylethylene, melting at 222° , besides acetic acid and 7.5 grams of unchanged benzhydrol acetate were the only reaction-products obtained.

A preliminary experiment with benzhydrol ethyl ether has shown that it decomposes on heating at 300° , in a distilling-flask, without air access, into acetaldehyde, tetraphenylethane, and benzophenone.¹

Finally, in this connection, I should like to make some remarks on the dissociation of dibenzyl sulphide, which has recently been worked out by Fromm and Achert.² These chemists obtained hydrogen sulphide, toluene, stilbene, thionessal (tetraphenylthiophene), and *s*-tetraphenylbutane as decomposition-products. The results are easily understood on the basis of a primary dissociation of benzyl sulphide into hydrogen sulphide and 2 molecules of phenylmethylene. Dibenzyl has also been noticed as a decomposition-product by previous observers, but not by Fromm and Achert. This was probably due to the fact that, in their experiments, the dibenzyl first formed was entirely alkylated by phenylmethylene as follows:



¹ Cf. Goldthwaite: *This JOURNAL*, 30, 447.

² *Ber. d. chem. Ges.*, 36, 534.

The following experiment, in which *s*-tetraphenylbutane is obtained from benzyl chloride by simply heating it with dry potassium oxalate, is evidence in favor of the view just presented.

An intimate mixture of 20 grams benzyl chloride and 35 grams anhydrous potassium oxalate was heated in an oil-bath, at 160°, for four hours. By treating the mass with water a small amount of solid remained undissolved. On crystallizing this from a mixture of acetone and alcohol, 1.8 grams of *s*-tetraphenylbutane, melting at 254° to 255°, were obtained in the form of pearly scales.

On the Action of Sodium on the Benzyl Esters of Acetic, Propionic, Butyric, and Isobutyric Acids—A Revision of Conrad and Hodgkinson's Work.—The experiments of Conrad and Hodgkinson on the action of sodium on the benzyl esters of the acids just named¹ whereby, apparently, the α -monobenzylated derivatives of these esters are obtained as the chief reaction-products have already been briefly discussed above. Such an alkylation is entirely in harmony with the data accumulated by Nef and with my own observations on the action of sodium or sodium benzhydrol on benzhydrol acetate and isobutyrate, respectively. The properties ascribed by Conrad and Hodgkinson to the esters obtained are, however, so unusual that it seemed very doubtful whether the substances actually prepared had the constitutions assigned to them. The esters in question are all mentioned as being capable of only very slight saponification, even after prolonged digestion with alcoholic potassium hydroxide, or by treatment with soda-lime at higher temperatures. The simplest way to test this point was obviously to synthesize benzyl hydrocinnamate, and then to compare it with the main reaction-product obtained by Conrad and Hodgkinson from sodium and benzyl acetate. This was accordingly done, and the synthetic product was found to behave in an entirely different manner toward alcoholic potassium hydroxide.

Synthesis and Properties of Benzyl Hydrocinnamate,
 $C_6H_5CH_2CH_2COOCH_2C_6H_5$. — Hydrocinnamic acid was con-

¹ Ann. Chem. (Liebig), 193, 298; 201, 166.

verted into the silver salt by neutralization with ammonia and precipitation with aqueous silver nitrate. The salt was purified by crystallization from hot water, well dried and then heated in a sealed tube, for eight hours, at 100° , with the calculated amount of benzyl chloride, diluted with 2 volumes of absolute ether. Benzyl hydrocinnamate was obtained as a colorless oil, boiling at 190° to 195° under 10 mm. pressure.

0.1527 gram substance gave 0.4463 gram CO_2 and 0.0920 gram H_2O .

	Calculated for $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{COOCH}_2\text{C}_6\text{H}_5$.	Found.
C	80.0	79.7
H	6.7	6.7

Ten grams of this oil were at once mixed with the theoretical amount of alcoholic potash and allowed to stand for two hours in the cold. Reaction took place at once, on working up the mixture 3.7 grams of benzyl alcohol, boiling at 204° to 208° , and 5 grams of hydrocinnamic acid, crystallized from ligroin and melting at 48° , were obtained. This striking ease of saponification of benzyl hydrocinnamate is not surprising in view of the statement of Erlenmeyer,¹ "the ethyl ester of hydrocinnamic acid is formed with marvellous ease, likewise it turns acid simply by contact with moist air."

Repetition of Conrad and Hodgkinson's Experiment with Sodium and Benzyl Acetate.—As mentioned above, benzyl acetate and sodium react, in absolute ethereal solution, at ordinary temperatures, giving chiefly sodium benzyolate and acetate besides small amounts of diacetyl and benzyl acetoacetate (not over 2 per cent).

A mixture of 100 grams benzyl acetate and 7 grams of sodium, cut in pieces about the size of a pea, does not interact in the cold. It was, therefore, heated, under a reversed condenser, in an oil-bath, with a thermometer in the mixture. As soon as the inside temperature reached 125° a reaction was noticed; the oil-bath was at once removed, the reaction proceeded with violence and the temperature rose to 185° . It is essential for success that there be a great rise of temperature,

¹ Ann. Chem. (Liebig), 137, 330.

as previous experiments have proved that, when smaller amounts of material are used and when care is taken to have the reaction proceed more slowly, practically no high boiling products at all are obtained. Even in the experiment just described my yield of high-boiling material was smaller, comparatively, than that given by Conrad and Hodgkinson. The reaction was completed in twenty minutes, and the dark-brown mixture in the flask was treated with dilute sulphuric acid and extracted with ether. The ether extract was then successively extracted with sodium carbonate and sodium hydroxide and thus resolved into acid and neutral products. One and one-tenth grams of cinnamic acid, melting at 131° , were found in the carbonate solution. The caustic alkali gave a small amount of oil having the properties of benzyl acetoacetate. The main reaction-products were found to be neutral in character, and were fractionated twice under 10 mm. pressure. A small amount of toluene, boiling at 105° to 108° under ordinary pressure, was obtained from the first fraction; then came 71 grams of oil boiling from 90° to 100° under 10 mm. pressure. This was obviously what Conrad and Hodgkinson considered to be unchanged benzyl acetate. It consists, however, chiefly of benzyl alcohol. The first fractions, 30 grams, had only the faintest odor of benzyl acetate. The 71 grams of oil obtained gave, furthermore, on treatment with 1.25 mol. alcoholic potassium hydroxide in the cold, 62 grams of pure benzyl alcohol, boiling at 204° to 206° . On further fractionation of the residue in the distilling-flask, 12 grams of oil, boiling at 160° to 190° under 10 mm. pressure, were obtained, and some tar. This oil was now digested for two hours with 3 grams alcoholic potash at 110° , and on working up for neutral and acid products, 3.4 grams of crude hydrocinnamic acid, boiling at 275° to 290° , were obtained. It soon solidified, and gave, on crystallization from ligroin (b. p. 70° to 80°), 3 grams of the pure acid melting at 47° . The neutral portion, distilled twice under 13 mm. pressure, gave 3.2 grams of benzyl alcohol, boiling at 95° to 100° , and 4 grams oil boiling at 155° to 165° . The latter was proved to be benzyl ether by comparison with a synthetic

product¹ (b. p. 167° to 168° under 15 mm. pressure), and also by analysis :

0.1922 gram substance gave 0.5962 gram CO₂ and 0.1245 gram H₂O.

	Calculated for (C ₆ H ₅ CH ₂) ₂ O.	Found.
C	84.8	84.6
H	7.1	7.2

From the above data it is obvious that two-thirds of the high-boiling oil consisted of benzyl hydrocinnamate and the remaining third of benzyl ether. Judging from their data, Conrad and Hodgkinson must have had relatively far more benzyl ether in their high-boiling oil. It should be emphasized here that benzyl ether burns with great difficulty ; furthermore, that, according to repeated observations of Nef, mixtures of benzyl alcohol and benzyl ether, containing also some phenyl methylene, are very hard to separate completely by fractional distillation under ordinary pressure. Finally, it is clear from the facts presented in this paper that the neutral and high-boiling products obtained by Conrad and Hodgkinson, after treatment with alcoholic potassium hydroxide, must, in all cases, have consisted largely of benzyl ether.

Benzyl Isobutyrate and Sodium Benzylate.—As the action of sodium on benzyl derivatives, in Conrad and Hodgkinson's experiments, obviously depends on the intermediate formation of sodium benzylate, and, owing to the resulting high temperature, on the subsequent alkylation by the phenylmethylene of the products present, the following experiment was carried out in the expectation that a benzylated isobutyric acid would result :

An intimate mixture of 20 grams benzyl isobutyrate and 15 grams sodium benzylate was heated in a sealed tube, for four hours, at 300° to 310°, and then worked up for acid and neutral products : 4 grams of isobutyric acid, 5.8 grams of benzoic acid melting at 122°, but no trace of an α -benzylated isobutyric acid was obtained. The neutral portion contained traces of benzaldehyde, as proved by the isolation of 0.2 gram

¹ Lowe : Ann. Chem. (Liebig), 241, 374.

of phenylhydrazone melting at 156° . The main products were, however, 6.1 grams of benzyl alcohol boiling at 94° to 100° under 10 mm. pressure, and benzyl ether, 8.1 grams, boiling at 130° to 170° under the same pressure. The latter was practically unaffected by digestion with alcoholic potash at 150° . On refractionation, under 8 mm. pressure, 2 grams of oil boiling at 150° to 159° , and 3.5 grams of oil boiling at 159° to 160° , were recovered. Analysis of the latter showed that it was pure benzyl ether.

0.1793 gram substance gave 0.5562 gram CO_2 and 0.1146 gram H_2O .

	Calculated for ($\text{C}_6\text{H}_5\text{CH}_2$) $_2\text{O}$.	Found.
C	84.8	84.6
H	7.1	7.1

According to Lowe (*loc. cit.*), benzyl ether gives toluene and benzaldehyde on prolonged heating at 315° . I have found that pure benzyl ether very slowly yields toluene and benzoic acid on prolonged digestion with alcoholic potassium hydroxide at 150° , or on heating with solid potassium hydroxide or soda-lime at 200° .

It is noteworthy that, in the reaction just described, a large amount of benzyl ether, but not a trace of α -benzylated isobutyric acid is obtained. The corresponding reaction with sodium benzhydrol and benzhydrol isobutyrate, at 300° , gave a 30 per cent yield of monoalkylated isobutyric acid (see above).

Finally, it is to be emphasized here that the substance described by Hodgkinson¹ as α -benzylated isobutyric benzyl ester is exceedingly stable toward alcoholic potash and never gave α -benzylated isobutyric acid by saponification under any conditions. I therefore consider it extremely probable, in view of the data just presented, that Hodgkinson's substance in reality consisted simply of benzyl ether. He succeeded, for instance, in obtaining from it, by means of soda-lime at 200° , toluene and benzoic acid.

In conclusion, I desire to thank Dr. Nef for his painstaking scrutiny and his inspiring interest in connection with this work.

¹ Ann. Chem. (Liebig), **201**, 166.

REVIEWS.

DIE GALVANOPLASTIK. Von DR. W. PFANHAUSER, Fabrikant von Maschinen, Apparaten, und Chemischen Präparaten für Elektroplattierung, Galvanoplastik, und Metallpolierung. Mit 35 in dem Text gedruckten abbildungen. Halle, a. S. : Verlag von Wilhelm Knapp. 1904. pp. 138.

This little monograph on applied electrochemistry deals with its subject under the following general heads. The various "forms" that are used, such as the metals, wax, gutta-percha, gypsum, etc., are considered.

The means of conducting the current are then discussed, such as covering the material in question with graphite or with a thin layer of metal.

The different baths that are employed, the choice of anodes, and the arrangement of apparatus are then taken up and treated at sufficient length to be clearly intelligible to any one who has even an elementary knowledge of technical electrochemistry. The monograph can be recommended to all who are interested in this subject.

H. C. J.

ELECTROLYTIC COPPER REFINING. By TITUS ULKE, M.E., Consulting Electrochemist. Member of the Amer. Electrochem. Soc. and Amer. Inst. Min. Engineers. New York : John Wiley & Sons. 1904.

DIE ELEKTROLYTISCHE RAFFINATION DES KUPFERS. Von TITUS ULKE. Ins Deutsche übertragen von VIKTOR ENGELHARDT, Ober-Ingenieur und Chemiker der Siemens & Halske, A. G., Wien. Halle, a. S. : Druck und verlag von Wilhelm Knapp. 1904. pp. 152. Price, 8 marks.

This small book is made up largely of articles which have been published in *Mineral Industry*. It contains a good deal of valuable information and is instructive to those who know enough about the refining of copper to enable them to weed out the true from the misleading statements.

I. R.

A LABORATORY MANUAL OF ORGANIC CHEMISTRY FOR BEGINNERS. By DR. A. F. HOLLEMAN, Professor Ordinarius in the University of Groningen, Netherlands, and Fellow of the Royal Academy of Sciences, Amsterdam. An Appendix to the Author's Text-book of Organic Chemistry. Translated from the Dutch by A. JAMIESON WALKER, PH.D. (Heidelberg), B.A., Head of the Department of Chemistry, Technical College, Derby, England, with the co-operation of the Author. New York : John Wiley & Sons ; London : Chapman & Hall, Limited. 1904. 12mo. pp. xiv + 78 Cloth. Price, \$1.00 net.

The author of this little book seems to think that the idea of working with the compounds of carbon in the laboratory as a part of a course in organic chemistry is rather a new one. It may be in the Netherlands. It is not elsewhere. The author's text-book of organic chemistry is an excellent book

and has been highly spoken of in this JOURNAL,¹ but the laboratory manual is much less satisfactory. A laboratory manual ought to be a safe guide for the student in the laboratory. If it leaves everything to the teacher, it fails of its purpose. The directions here given are so meager that a student would certainly fail in his efforts to perform the experiments unless his teacher should give him a lot of supplementary directions. Take acetaldehyde, for example, page 20. These are the directions: "A mixture of 60 grams of water, 20 grams of concentrated sulphuric acid, and 15 grams of 90 per cent alcohol is added to 13 grams of potassium dichromate contained in a 200 cc. fractionating flask connected with a condenser. Sometimes the oxidation begins spontaneously. Should it not, however, the flask is gently heated on a sand-bath, with a rapid current of cold water flowing through the condenser. A mixture of water, alcohol, acetaldehyde, and acetal distils, and can be used in carrying out the aldehyde-reactions described in 2, 3, and 4." If the experience of thirty odd years is worth anything, that experiment is doomed to failure.

Under formic acid nothing is said about the temperature to which the mixture of glycerol and oxalic acid is to be heated. Similar criticisms are applicable to practically all the directions given in the book. It is hard to see what purpose it will serve that is not much better served by several other books already in use.

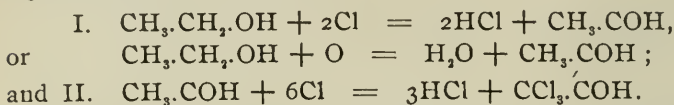
I. R.

DIE ELEKTROCHEMISCHE REDUKTION DER NITRODERIVATE ORGANISCHER VERBINDUNGEN IN EXPERIMENTELLER UND THEORETISCHER BEZIEHUNG. By JOH. MÖLLER. Halle, a. S.: Wilhelm Knapp. 1904.

This small book of 113 pages, exclusive of the excellent index, gives an interesting account of the results that have been attained in its field. The application of the electric current in organic synthesis has been developed chiefly during the last seven years, and at present a large number of important substances are prepared in this way. Mixed azo compounds and many others can be obtained with greater ease, or in some cases, only by this method. The points of chief importance are the proper selection of current strength, the character and material of the electrodes, and, at times, the use of different condensing agents to stop the action at the desired phase. According to the conditions, the products may be either primary or secondary. In the first case the ions, after losing their charges, combine with one another, as in

¹ This JOURNAL, 31, 190.

Kolbe's classical synthesis of ethane by the electrolysis of potassium acetate solution. When of a secondary nature, the products are formed by the oxidation or reduction of the discharged ions, or by the action of other substances that may be present in the solution. For instance, when alcoholic solution of potassium chloride is electrolyzed, chloral is obtained probably according to the equations :



In like manner, when nitrobenzene, in solution of alcoholic hydrochloric acid, is hydrolyzed, phenyl hydroxylamine is obtained which is then acted on by hydrochloric acid, giving phenyl chloramine. The method evidently is one with great possibilities for nitroso, hydroxylamine, azoxy, azo, hydrazo, amino, aminoxy, diaminodiphenyl, and benzidine derivatives are obtained when nitro compounds are electrolyzed. With the exception of the last class, all of these can be formed in alkaline, as well as in acid solution.

In the first part of the book the methods employed in carrying out reductions in acid and alkaline solution are given in detail. Then follows a discussion of the theories proposed by Haber,¹ Chilesotti,² and Löb,³ to account for the observed phenomena.

The book is one that should be in the hands of every one who wishes to become informed on the subject. It is clearly written, and there are numerous references to the literature. It is hardly necessary to say that it is well printed.

C. E. W.

¹ Ztschr. Elektrochem., 1897-98, p. 506.

² *Ibid.*, 1900-01, p. 768.

³ "Unsere Kenntnisse in der Elektrolyse und Elektrosynthese organischer Verbindungen," p. 63.

AMERICAN CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of the University of Illinois.

PRIMARY ARSINES.

BY WILLIAM M. DEHN.

THEORETICAL.

The elements of the nitrogen group yield characteristic trihydrogen, trihalogen and pentahalogen derivatives. Most of the compounds of these series have been prepared and studied, but a few, particularly some of the pentahalides, are yet unknown.

All of the pentahalogen compounds of phosphorus, except the iodide and of antimony, except the bromide, have been prepared. Only the pentachloride of arsenic is known,¹ although the iodide was probably obtained by Sloane². Nitrogen and bismuth, the two extremes of the nitrogen group, have both resisted the efforts of chemists to prepare their pentahalogen derivatives. All of the known pentahalides are unstable, especially at elevated temperatures and in the presence of water. This instability accounts for the difficulty of their preparation.

¹ J. Am. Chem. Soc., 24, 1070; 26, 632.

² Chem. News, 46, 196.

The trihalides of the nitrogen family, on the other hand, are usually stable, consequently we find that most of them have been obtained. The only unknown trihalogen compound is the fluoride of nitrogen, with the corresponding bromide doubtful.¹

The hydrides of the nitrogen elements are compounds of considerable stability which decreases, however, with increase of the atomic weight of the element combining with hydrogen. Although ammonia, phosphine and arsine are stable in the presence of water and at ordinary temperatures, stibine is slowly decomposed by water² and suffers partial decomposition at a temperature even as low as -60° .³

Though there are a number of gaps in the above-mentioned series of compounds of the nitrogen elements, it seems very probable that, when investigators have the time and inclination to determine the conditions of their formation and existence, we shall find perfectly analogous series in the hydride and halogen compounds.

Striking similarities between the elements of the nitrogen group are especially recognizable in the alkyl substitution-products of their hydrides. For a number of years the complete analogy of the phosphorus alkyl compounds to those of nitrogen has been acknowledged. The research of A. W. Palmer on the secondary arsines⁴ and the completion of this work on the primary arsines⁵, have extended this analogy to the alkyl substituents of the arsenic hydrides.

The existence of the alkyl amines was predicted by Liebig as early as 1842.⁶ Seven years later Würtz prepared the primary amines.⁷ In 1851 A. W. Hofmann discovered the method by which the three classes of amines and the alkyl ammonium bases may be formed simultaneously.⁸ Upon working out their separation, more than half a

¹ Ann. Chem. (Liebig), **69**, 75.

² J. Am. Chem. Soc., **1**, 641 (1876).

³ Monatsh. Chem., **5**, 127.

⁴ Ber. d. chem. Ges., **27**, 1378.

⁵ A. W. Palmer and W. M. Dehn : *Ibid.*, **34**, 3594.

⁶ Handwörterbuch, **1**, 689.

⁷ Ann. Chem. (Liebig), **71**, 330 ; **76**, 318.

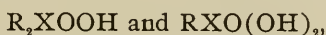
⁸ *Ibid.*, **79**, 19.

century ago, he established the existence of primary, secondary and tertiary amines.

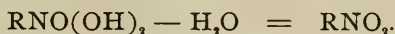
Though phosphine is much less basic than ammonia it forms alkyl substituents perfectly analogous to those of the amines. The first representative of these compounds, tertiary phosphine, was prepared in 1846, by Thénard.¹ The existence of the primary and secondary phosphines was not established until 1871, when Hofmann² condensed phosphonium iodide and alkyl iodides by means of zinc oxide, obtaining both primary and secondary phosphines in the reaction products. Representatives of all the phosphines have, therefore, been known for over thirty years.

Arsine differs from ammonia and phosphine in being devoid of basic properties, but, like the other two, it forms all classes of alkyl substitution products. Tertiary alkyl arsine has been known since 1858, when it was discovered by Hans Landolt.³ He prepared it by treating sodium arsenide with alkyl iodide. A secondary arsine was first prepared by Palmer, in 1894,⁴ by reducing cacodyl chloride with zinc and hydrochloric acid in alcoholic solution. Two years ago the discovery of the primary arsines was announced from this laboratory.⁵ Since 1901 the study of these bodies has been continued, a representative series of them has been prepared and their reactions studied.

Phosphorus, arsenic and antimony form mono- and dialkyl acids of the types :



in which X is the element of the nitrogen group. Nitrogen apparently differs from the three in not forming acids of these types. The nitro bodies, however, may be considered as being derived from acids of the second type :



The polybasic nitrogen acids are unstable; if a nitrogen acid of the above type were formed it would change easily into the

¹ Berz. Jahresber., 26, 598.

² Ber. d. chem. Ges., 4, 430.

³ Ann. Chem. (Liebig), 89, 321.

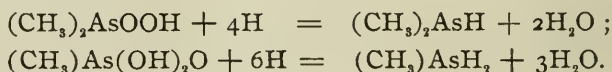
⁴ Ber. d. chem. Ges., 27, 1378.

⁵ *Ibid.*, 34, 3594.

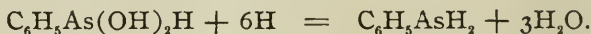
nitro compound. A striking analogy between the nitro bodies and the acids of the above type is observed in the aromatic arsonic acids. On being heated these lose one molecule of water and change to nitro-like compounds.¹ That the nitro bodies are really anhydrides of acids is seen in the weakly acid properties of the nitroparaffines. There is, therefore, complete analogy among the mono-alkyl acids of nitrogen, phosphorus, arsenic and antimony.

No dialkyl representatives among the nitrogen acids are found; the R_2N group being more positive than the RN group, there is less possibility of the existence of an acid of the R_2NOOH type than of the $RN(OH)_2O$ type, but in the dialkyl nitro amines and the dialkyl nitroso amines we have the R_2N group united with NO_2 and NO groups, respectively. These compounds, in their reducibility, show some similarity to the dialkyl acids of phosphorus, arsenic and antimony, and may be considered the nearest approach of nitrogen to acids of the second type.

I have found that the arsenic acids of the two types mentioned above reduce smoothly, by means of zinc and hydrochloric acid, to secondary and primary arsines respectively. For instance :



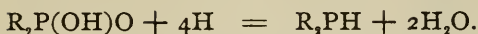
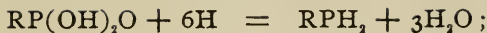
The reduction takes place with equal ease in the aromatic series, monophenyl arsine, the analogue of aniline, being obtained from phenyl arsonic acid,



A general and easy method for the preparation of primary and secondary arsines is thus afforded. This reduction is perfectly analogous to the reduction of aromatic nitro bodies and the nitro paraffins.² Though none of the phosphines have been prepared by the application of this general reaction, it is very probable that alkyl phosphoric acid and dialkyl phosphinic acids will reduce in the same manner :

¹ Ann. Chem. (Liebig), **320**, 277.

² Ber. d. chem. Ges., **24**, 3528, 4243; **25**, 1714.



In the aliphatic series these acids are mostly derived from the phosphines,¹ but in the aromatic series the acids themselves are readily obtainable, and their reduction ought to afford an easier preparation of the phosphines than the present methods. These reactions will be studied in this laboratory in the immediate future.

None of the corresponding acids of antimony are known in the aliphatic series, but in the aromatic series representatives of both acids have been prepared.² Their difficult solubility, at least in the case of phenyl stibine acid, precludes their use in the preparation of primary and secondary stibines, but mono- and dialkyl substituents of the trihalides may be employed, at least in the aromatic series. By their reduction I have prepared mono- and diphenyl stibine, though as yet not in a state sufficiently pure for analysis. Studies of these compounds are now being made and the results will be announced during the year.

Palmer³ prepared dimethyl arsine by reducing dimethyl arsine chloride. Treatment of phenyl arsine dichloride with zinc and hydrochloric acid develops immediately the odor of phenyl arsine. Evidently the mono and dialkyl substituents of arsenic trihalides readily reduce to the respective arsines. Though none of the analogous substituents of phosphorus and nitrogen trihalides have been employed, it seems very probable that they would, in a similar manner, reduce to the primary and secondary phosphines and amines.

Evidently the primary and secondary amines, phosphines, arsines and stibines are derivable from their respective mono and dialkyl acids and halogen substituents. In other words, *an aqueous or alcohol solution of any mono or dialkylated nitrogen, phosphorus, arsenic, or antimony compound will reduce to the respective amine, phosphine, arsine, or stibine when in contact with nascent hydrogen evolved from zinc and hydrochloric acid.* This point is of great interest because it shows, in a

¹ Ber. d. chem. Ges., 4, 610; 5, 106; 6, 304.

² *Ibid.*, 31, 2913; Ann. Chem. (Liebig), 233, 59.

³ Ber. d. chem. Ges., 27, 1378.

striking manner, the close analogies existing among the nitrogen elements.

A study of the physical properties of the organic derivatives of ammonia, phosphine, arsine and stibine reveals closely analogous properties. The aliphatic amines, phosphines, arsines and stibines are all mobile, transparent, colorless oils of high refractive power. The aromatic bodies are either colorless solids or heavy oils of high refractive power.

In the table (p. 107) I have brought together the various boiling-points; it shows at a glance the known compounds and those which have not yet been prepared; it also indicates the influence on the boiling-points of the different elements of the nitrogen series and of the various organic groups, respectively. Undoubtedly some of the irregularities observable are due to inaccurate determinations. An item of interest, discovered by Hofmann,¹ is the identity of boiling-points of the isomers—dimethyl phosphine and ethyl phosphine. A similar identity is noticed also in the case of dimethyl arsine and ethyl arsine.

It will be seen in the table (p. 108) that the specific gravities of the fatty amines and phosphines are all less, while the specific gravities of all the others are probably greater than that of water.

The solubilities of these compounds have been studied only slightly. Methyl amine is soluble to the extent of 1150 volumes in water at 12°.5, and 595 volumes at 25°. These volumes, converted into weights, are 16000 and 13200 parts of amine soluble in 10000 parts of water. Methyl arsine and ethyl arsine are soluble about 1 part in 10000 at 25°. So the amines are 10000–15000 times more soluble in water than the arsines. No direct measurements of the solubilities of the phosphines in water have been made, though they are described as practically insoluble.² Aniline is soluble in 31 parts of water at 12°.5. It will be seen from the above meager data, and a comparative study of their basic properties, that the solubilities of these compounds in water increase with the degree of their basicity.

¹ Ber. d. chem. Ges., 4, 610.

² *Ibid.*, 4, 608.

Boiling-Points.

	Amines.	Phosphines.	Arsines.	Stibines.	Bismuth- ines.
Methyl :					
a. Primary	$-6^{\circ 1}$	$-14^{\circ 10}$	$2^{\circ 19}$	. .	. .
b. Secondary	$7^{\circ 2}$	$25^{\circ 11}$	$36^{\circ 20}$	. .	. .
c. Tertiary	$35^{\circ 3}$	$40^{\circ}-42^{\circ 12}$	$70^{\circ 21}$	$80^{\circ}.6^{26}$	$110^{\circ 29}$
Ethyl :					
a. Primary	$18^{\circ}.5^4$	$25^{\circ 13}$	$36^{\circ 22}$	. .	. .
b. Secondary	$55^{\circ}.5^5$	$85^{\circ 14}$	. .	. .	. .
c. Tertiary	$89^{\circ 6}$	$127^{\circ}.5^{15}$	$140^{\circ 23}$	$158^{\circ}.5^{27}$	$107^{\circ 30}$
					(79 mm.)
Phenyl :					
a. Primary	$183^{\circ}.7^7$	$161^{\circ 16}$	$148^{\circ 24}$	. .	. .
b. Secondary	$302^{\circ 8}$	$280^{\circ 17}$	. .	. .	. .
c. Tertiary m.p.	$127^{\circ 9}$	$360^{\circ 13}$	$360^{\circ 25}$	$360^{\circ 23}$	m.p. $78^{\circ 31}$

¹ Ber. d. chem. Ges., 22, 701.² Ibid., 22, 702.³ Ibid., 22, 703.⁴ Ann. chim. phys. (3), 30, 471; Ber. d. chem. Ges., 22, 704.⁵ Roy. Soc. Proc., 11, 67; R. 1, 59; Ber. d. chem. Ges., 22, 705.⁶ Ann. Chem. (Liebig), 200, 186; Ber. d. chem. Ges., 22, 705.⁷ J. Chem. Soc., 37, 221.⁸ Ann. Chem. (Liebig), 238, 363.⁹ Ber. d. chem. Ges., 6, 1514.¹⁰ Ibid., 4, 608.¹¹ Ibid., 4, 610.¹² Ann. Chem. (Liebig), 104, 29.¹³ Ber. d. chem. Ges., 4, 432.¹⁴ Ibid., 4, 433.¹⁵ Ibid., 4, 207.¹⁶ Ann. Chem. (Liebig), 181, 341.¹⁷ Ber. d. chem. Ges., 15, 801; 21, 1508.¹⁸ Ibid., 15, 802; Ann. Chem. (Liebig), 229, 299.¹⁹ Ber. d. chem. Ges., 34, 3597.²⁰ Ibid., 27, 1378.²¹ Jahresber., 1855, p. 538.²² Vide, p. 143.²³ Ann. Chem. (Liebig), 89, 321.²⁴ Ber. d. chem. Ges., 34, 3599.²⁵ Ann. Chem. (Liebig), 201, 237; Ber. d. chem. Ges., 15, 2876.²⁶ Jahresber., 1861, p. 569.²⁷ Ann. Chem. (Liebig), 75, 315; Jahresber., 1860, p. 373; Ibid., 1863, p. 470.²⁸ Ann. Chem. (Liebig), 233, 43.²⁹ Ber. d. chem. Ges., 20, 1517.³⁰ Ibid., 20, 1519.³¹ Ibid., 20, 55; Ann. Chem. (Liebig), 251, 324.

Specific Gravities.

	Amines.	Phosphines.	Arsines.	Stibines.	Bismuth- ines.
Methyl:					
a. Primary	0.699 ¹ (—10°.8)	less than ⁹ I	?	. .	. .
b. Secondary	0.6865 ² (—5°.8)	less than ¹⁰ I	1.213 (29°)	. .	. .
c. Tertiary	0.662 ³ (—5°.2)	? ¹¹	?	1.523 ²¹ (15°)	2.30 ²⁴ (18°)
Ethyl:					
a. Primary	0.708 ⁴ (—2°)	less than ¹² I	1.217 ¹⁸ (22°)	. .	. .
b. Secondary	0.7107 ⁵ (15°)	less than ¹³ I	. .	. .	. .
c. Tertiary	0.735 ⁶ (15°)	0.812 ¹⁴ (15°)	1.151 ¹⁹ (16°.7)	1.3244 ²² (16°)	1.82 ²⁵
Phenyl:					
a. Primary	1.0361 ⁷ (0°)	1.001 ¹⁵ (15°)	?	. .	.
b. Secondary	1.159 ⁸	1.07 ¹⁶ (16°)	. .	. .	. .
c. Tertiary	?	1.194 ¹⁷	1.306 ²⁰	1.4998 ²³ (12°)	1.5851 ²⁶ (20°)

¹ Ber. d. chem. Ges., 22, 701.² *Ibid.*, 22, 702.³ *Ibid.*, 22, 703.⁴ *Ibid.*, 22, 704.⁵ *Ibid.*, 22, 704.⁶ *Ibid.*, 22, 705.⁷ Kopp.⁸ Ber. d. chem. Ges., 12, 563.⁹ *Ibid.*, 4, 608.¹⁰ *Ibid.*, 4, 610.¹¹ Ann. Chem. (Liebig), 104, 29.¹² Ber. d. chem. Ges., 4, 432.¹³ *Ibid.*, 4, 433.¹⁴ Ann. Chem. (Liebig), Suppl., 1, 4.¹⁵ *Ibid.*, 181, 341.¹⁶ Ber. d. chem. Ges., 21, 1508.¹⁷ *Ibid.*, 15, 802.¹⁸ *Vide*, p. 143.¹⁹ Ann. Chem. (Liebig), 89, 321.²⁰ *Ibid.*, 201, 237.²¹ Jahresber., 1861, p. 569.²² Ann. Chem. (Liebig), 75, 315.²³ *Ibid.*, 233, 43.²⁴ Ber. d. chem. Ges., 20, 1517.²⁵ *Ibid.*, 20, 1519.²⁶ Ann. Chem. (Liebig), 251, 329.

All of the amines, phosphines and arsines are readily soluble in alcohol and ether.

The odors of these compounds, though varying greatly, are penetrating and very disagreeable. The ethyl derivatives are more unpleasant than the methyl and phenyl and apparently the compounds of the heavier elements of the group possess the more disagreeable odors. The fatty arsines have odors resembling cacodyl, but they are quite easily distinguishable. Phenyl arsine, in a concentrated form, is very disagreeable, but on dilution, its odor, like triethyl phosphine,¹ resembles hyacinth.

Most of these substances, particularly the phosphines and arsines, are powerful poisons. Their spontaneous oxidation to comparatively innocuous products prevents fatalities to the investigator.

In chemical behavior, however, the compounds show remarkable dissimilarities. The aliphatic alkylated phosphines and arsines are distinguished from the corresponding ammonia derivatives by their ready oxidizability; they absorb oxygen by mere exposure to the air; whereas the secondary phosphines² and arsines³ are spontaneously inflammable, the primary compounds manifest this property only on moderate warming.⁴ With increase of atomic weight of the nitrogen elements, the tertiary derivatives show a gradual increase of inflammability and explosibility. The oxide of trialkyl amines can be formed only indirectly,⁵ the tertiary phosphines unite directly with the oxygen of the air, the arsines and stibines fume and inflame, and the bismuth compounds inflame and explode.⁶ These tertiary aliphatic derivatives are very sensitive towards atmospheric oxygen, but the tertiary aromatic compounds of all the nitrogen elements are stable in air. The primary and secondary aromatic compounds manifest dissimilarities. Aniline is only slowly acted upon by air, though it is very sensitive to other oxidizing agents. The analogous phosphorus⁷

¹ Ann. Chem. (Liebig), 104, 10.

² Ber. d. chem. Ges., 4, 431, 610.

³ *Ibid.*, 27, 1378.

⁴ *Ibid.*, 6, 302.

⁵ J. russ. physik. chim. Gesell., 20, 126.

⁶ Ber. d. chem. Ges., 20, 1517.

⁷ Ann. Chem. (Liebig), 181, 344.

and arsenic compounds, however, are oxidized quickly in the air.

The products of these spontaneous oxidations are in most cases analogous. The tertiary compounds simply add oxygen, forming bodies of the type R_3XO .¹ The secondary phosphines and arsines yield their respective dialkyl acids.² In the case of the primary bodies, however, differences between the phosphines and arsines are noticeable; whereas the phosphines evidently give rise to the monoalkyl acids,³ the primary arsines form, in addition, polymerized products. Phenyl arsine yields arseno-benzene;⁴ methyl arsine, a red, glistening product;⁵ ethyl arsine a light-yellow substance. All of these condensed compounds dissolve in nitric acid, forming the corresponding monoalkyl arsonic acids.

Though little or no study has been made of the action of nitric acid on the amines, other oxidizing agents yield the most varying products, especially with aniline. With dilute nitric acid all of the primary and secondary phosphines⁶ and arsines are oxidized smoothly to the corresponding alkyl acids; with concentrated nitric acid, however, secondary reactions take place. In the aliphatic series the alkyl groups are eliminated from arsenic, and the two constituents are oxidized, the alkyl to the corresponding fatty acid, the arsenic to a mixture of arsenious and arsenic acids. In the aromatic series, secondary reactions give rise to nitrobenzene or its homologues, together with the arsenic acids.

The most characteristic differences among the various amines, phosphines and arsines are seen in their varying basic properties. Though none but the fatty amines affect red litmus, the tendency of the others to form salts shows a retention of basic properties. The alkyl groups being positive, the amines possess greater basic properties than ammonia.⁷ Ost-

¹ Z. physik. Chem., **22**, 35; Ber. d. chem. Ges., **30**, 1673.

² *Ibid.*, **15**, 801; **21**, 1508.

³ *Ibid.*, **7**, 1689; **10**, 808.

⁴ *Ibid.*, **14**, 3599.

⁵ *Ibid.*, **34**, 3596.

⁶ *Ibid.*, **5**, 109; **6**, 304; **15**, 802.

⁷ J. prakt. Chem., [2], **33**, 352.

wald¹ gives the following relative affinities, determined by the electrolytic method :

NH_3	4.8
CH_3NH_2	20.2
$(\text{CH}_3)_2\text{NH}$	23.5
$(\text{CH}_3)_3\text{N}$	9.7
$(\text{C}_2\text{H}_5)\text{NH}_2$	20.5
$(\text{C}_2\text{H}_5)_2\text{NH}$	28.3
$(\text{C}_2\text{H}_5)_3\text{N}$	20.2
$(\text{C}_2\text{H}_5)_4\text{NOH}$	128.0

The aromatic groups being negative, the basic properties of the aromatic amines decrease with the number of groups introduced. The primary salts are stable, the secondary are decomposed by water and the tertiary ones are apparently incapable of existing.

Whereas the primary phosphines² and phosphine itself are so weakly basic that their salts are unstable in the presence of water, the introduction of alkyl groups strengthens them in this property, so that secondary phosphines are decomposable only by means of alkalis.³ Tertiary phosphines react like well characterized bases.⁴ As most of the salts of the aromatic amines are unstable and the phosphines are less basic than the amines, it is easily understood why the salts of all the aromatic phosphines are decomposed by water.⁵ From the fact that arsine itself is devoid of basic properties and that no tertiary arsine salts have been prepared, it would appear that all the arsines are devoid of basic properties. I have, however, obtained double compounds of ethyl arsine and sulphuric acid, and dimethyl arsine and sulphuric acid, which are evidently salts. They are decomposable by water, giving an arsine-like odor. (*Vide*, p. 144.)

Of considerable theoretical interest is the action of the halogens on the various amines, phosphines and arsines. By their action, alone or in the presence of caustic alkalis, the primary and secondary aliphatic amines yield alkylamine halides.⁶

¹ J. prakt. Chem., [2], 35, 121.

² Ann. Chem. (Liebig), 181, 344.

³ Ber. d. chem. Ges., 4, 434.

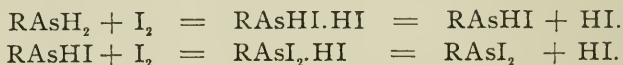
⁴ Ann. Chem. (Liebig), 104, 12.

⁵ Ber. d. chem. Ges., 12, 1509; Ann. Chem. (Liebig), 229, 304.

⁶ Ber. d. chem. Ges., 8, 1470; 9, 146; 16, 558; 23, R. 386; Ann. Chem. (Liebig),

These, like the inorganic nitrogen halides, are very unstable, for instance dialkyl chloramine, which is more stable than the mono-alkyl compound, easily changes into dialkyl ammonium chloride.¹ Aromatic amines are substituted in the ring by the action of halogens. Aromatic amine chlorides, in which halogens have substituted the amine hydrogen, are apparently incapable of existence. Unlike the amines, the phosphines and arsines, both aliphatic and aromatic, are acted upon by the halogens with the greatest ease. Hofmann² found that the aliphatic phosphines unite with halogens with explosive violence, but he did not study their reaction-products. The aromatic products have been studied with but little success.

I have made some studies of the action of dry halogens on primary arsines, which indicate that the end-products are alkylarsine dihalides, but there is evidence that intermediate addition compounds are formed. As shown below (p. 151), it is probable that the reactions are as follows :



The following table exhibits all the possible intermediate and final products. Representatives of compounds marked with the asterisk are known.

*RNH ₂	*RPH ₂	*RAsH ₂
RNHX.HX	RPHX.HX	RAsHX.HX
*RNHX ³	RPHX	RAsHX
RNX ₂ HX	RPX ₂ HX	RAsX ₂ HX
*RNX ₂ ⁴	*RPX ₂ ⁵	*RAsX ₂ ⁷
RNX ₄	*RPX ₄ ⁶	RAsX ₄

At present the above pentavalent compounds of nitrogen and arsenic are unknown. With the increase of alkyl groups, the capacity of the nitrogen groups for halogens increases, as will be seen by a study of the following dialkyl compounds :

¹ Ann. chim. phys. [7], 3, 320.

² Ber. d. chem. Ges., 4, 433 ; 6, 302.

³ Ann. chim. phys. [7], 3, 318-321.

⁴ Ber. d. chem. Ges., 9, 146 ; 12, 771 ; 28, 1683 ; 32, 3343 ; 32, 3582 ; Ann. Chem. (Liebig), 230, 222 ; Z. physik. Chem., 16, 214 ; Ber. d. chem. Ges., 15, 767.

⁵ Ibid., 13, 2174 ; 32, 1574.

⁶ Ibid., 13, 2174 ; 32, 1574.

⁷ Ann. Chem. (Liebig), 107, 285 ; 249, 152.

$*R_2NH$	$*R_2PH$	$*R_2AsH$
$*R_2NX.HX^1$	$R_2PX.HX$	$R_2AsX.HX$
$*R_2NX^2$	R_2PX	$*R_2AsX^4$
$*R_2NX_3^3$	R_2PX_3	$*R_2AsX_3^5$

Here all of the intermediate products of nitrogen are known and the formation of the unknown phosphorus derivatives is very probable.

The alkyl groups increase the basic properties, but introduction of halogen decreases them; therefore $CH_3NI.HI$ would be an unstable salt, and $CH_3NI_2.HI$ even more so. The corresponding phosphorus and arsenic salts would be still less stable because compounded of weaker bases. The aromatic radicals being negative there is a greater tendency for their compounds with the heavier nitrogen elements to react with halogens. In the following table R represents aromatic groups and X the halogens:

$*RNH_2$	$*RRH_2$	$*RAsH_2$
$RNHX.HX$	$RPHX.HX$	$RAsHX.HX$
$RNHX$	$RPHX$	$RAsHX$
$RNX_2.HX$	RPX_2HX	$RAsX_2HX$
RNX_2	$*RPX_2^6$	$*RAsX_2^8$
RNX_4	$*RPX_4^7$	$*RAsX_4^9$

There is evidence that one of the three unknown intermediate compounds of arsenic can be formed (*vide*, p. 151). The following table represents the secondary aromatic compounds:

$*R_2NH$	$*R_2PH$	$*R_2AsH$
$R_2NX.HX$	$R_2PX.HX$	$R_2AsX.HX$
R_2NX	$*R_2PX^{10}$	$*R_2AsX^{12}$
R_2NX_3	$*R_2PX_3^{11}$	$*R_2AsX^{13}$

¹ Ann. Chem. (Liebig), 18, 94; 20, 60.

² *Ibid.*, 230, 223.

³ Ber. d. chem. Ges., 18, 2249.

⁴ Ann. Chem. (Liebig), 92, 364; 116, 367.

⁵ *Ibid.*, 107, 267; 116, 367.

⁶ *Ibid.*, 181, 280; 212, 205, 236; 293, 292; 294, 2, 35, 48, 54; Ber. d. chem. Ges., 9, 1051; 11, 1500; 13, 1624; 20, 1720; 21, 1494.

⁷ Ann. Chem. (Liebig), 181, 294; 294, 2, 35, 48; Ber. d. chem. Ges., 9, 1519; 31, 2915; 20, 1720.

⁸ Ber. d. chem. Ges., 14, 913; 15, 2876; Ann. Chem. (Liebig), 201, 191.

⁹ Ann. Chem. (Liebig), 201, 191.

¹⁰ Ber. d. chem. Ges., 10, 627; 18, 2109.

¹¹ *Ibid.*, 10, 627.

¹² Ann. Chem. (Liebig), 201, 215, 230; 207, 115; 233, 91; Ber. d. chem. Ges., 11, 1503.

¹³ Ann. Chem. (Liebig), 207, 115.

The tertiary amines and phosphines, both aliphatic and aromatic, show little or no tendency to form addition products with halogens. Only the dichloride of triphenyl phosphine is recorded as conjectural.¹ Arsenic yields only unstable tertiary addition products,² while the corresponding dihalides of antimony³ and bismuth,⁴ are well defined and stable.

The primary and secondary aliphatic phosphines react at ordinary temperatures with the alkyl halides, forming well-characterized halogen salts of the higher alkyl phosphines.⁵ The tertiary phosphines, both aliphatic⁶ and aromatic,⁷ give rise to the most varied phosphonium bases. It has been known for a long time that both aliphatic⁸ and aromatic tertiary⁹ arsines yield the corresponding arsonium iodides, when treated with alkyl halides. Even tribenzylarsine yields tetrabenzylarsonium chloride when heated at 175° with benzyl chloride.¹⁰ This property of adding alkyl halides is noticeable in the case of the tertiary aromatic stibines, but not in that of aliphatic stibines.

I have found that primary arsines unite with alkyl halides as readily as do the amines and phosphines, and I have obtained, as end-products, nearly quantitative yields of the arsonium iodides. Both the aliphatic and the aromatic arsines and halides react in this manner. Therefore a general method is afforded for the preparation of arsonium compounds in which all the groups are alike, R_4AsI , or of those of the general form, $R_3R''AsI$, in which three of the groups are alike and the fourth different. By the distillation of these compounds, various tertiary arsines may be prepared, which, on treatment with other alkyl halides, give rise to arsonium compounds of the general form, $R'R''R'''AsI$. The secondary arsines will undoubtedly react in the manner of the primary

¹ Ber. d. chem. Ges., 15, 802.

² Ann. Chem. (Liebig), 92, 365; 110, 228; 201, 62, 233, 237.

³ *Ibid.*, 97, 329; 103, 306; 233, 43; 242, 176; Jahresber., 1860, p. 374; 1863, p. 470.

⁴ Ann. Chem. (Liebig), 251, 329; Ber. d. chem. Ges., 20, 56.

⁵ Ber. d. chem. Ges., 6, 299.

⁶ Ann. Chem. (Liebig), 104, 16-31; Spl., 1, 154; 53, 710; Jahresber., 1860, p. 341; 1861, p. 487.

⁷ Ann. Chem. (Liebig), 181, 362; 207, 210; 229, 310; Ber. d. chem. Ges., 15, 198, 803, 2018; 27, 277; 31, 2920; 53, 724; Jahresber., 1883, p. 1307.

⁸ Ann. Chem. (Liebig), 89, 331; Spl., 1, 311.

⁹ *Ibid.*, 201, 212; 207, 196, 205; 233, 78.

¹⁰ *Ibid.*, 233, 78.

arsines, when heated with alkyl halides and will give arsonium compounds of the general form, $R_2R'_2AsI$. Finally, by a combination of the above principles, arsonium iodides of the general form, $R'R''R'''R''''AsI$, may be prepared.

Following is a list of the arsonium compounds known hitherto :

- 1 $(CH_3)_4AsI^1$
- 2 $(C_2H_5)_4AsI^2$
- 3 $(CH_3)_2(C_2H_5)_2AsI^3$
- 4 $(CH_3)_2(C_5H_{11})_2AsI^4$
- 5 $(C_2H_4Br)(C_2H_5)_3AsBr^5$
- 6 $C_6H_5(CH_3)_3AsI^6$
- 7 $(C_6H_5)_2(CH_3)_2AsI^7$
- 8 $(C_6H_5)_2(C_2H_5)_2AsI^8$
- 9 $C_6H_5(C_2H_5)_3AsI^9$
- 10 $(C_6H_5)_2CH_3 \cdot C_2H_5AsI^{10}$
- 11 $(C_6H_5CH_2)_4AsI^{11}$
- 12 $C_6H_5CHCl(CH_3)_2 \cdot C_6H_5AsI^{12}$

I have prepared the following compounds, which can be added to *ad libitum* :

- 13 $(CH_3)_3C_2H_5AsI$
- 14 $CH_3(C_2H_5)_3AsI$
- 15 $C_6H_5(C_5H_{11})_3AsI$
- 16 $C_2H_5(C_5H_{11})_3AsI$
- 17 $C_2H_5(C_3H_7)_3AsI$

As is well known, the Hofmann reaction gives mixtures of the amines. The explanation of this is that the free base, either ammonia or the amine, partially decomposes the salts formed, thus giving opportunity for the alkyl halide to add again. That the arsines, with alkyl halides, give at once quarternary compounds, can be explained by the instability of the primary,

¹ Ann. Chem. (Liebig), **92**, 361 ; **122**, 192 ; **116**, 364 ; Z. physik. Chem., **13**, 301.

² Ann. Chem. (Liebig), **89**, 331 ; **92**, 364.

³ *Ibid.*, **92**, 362 ; **122**, 209.

⁴ *Ibid.*, **92**, 364.

⁵ *Ibid.*, Spl., **1**, 311.

⁶ *Ibid.*, **207**, 205.

⁷ *Ibid.*, **207**, 199.

⁸ *Ibid.*, **201**, 235.

⁹ *Ibid.*, **201**, 212.

¹⁰ *Ibid.*, **207**, 196.

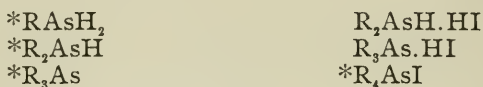
¹¹ *Ibid.*, **233**, 78.

¹² Ber. d. chem. Ges., **25**, 1521.

secondary and tertiary salts. If these are formed they decompose immediately into free arsines and with more alkyl halide build up rapidly into arsonium compounds.

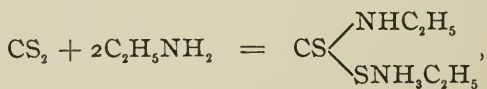
By heating, I invariably obtain arsonium iodides. In the cold, however, other possibilities arise.

I have evidence that some of the following, hitherto unknown, compounds are formed :

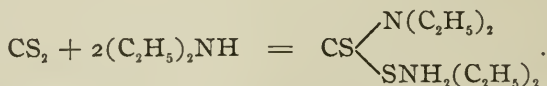


When methyl and ethyl arsines are treated, at the ordinary temperature, with ethyl or methyl iodide, needle-like or flaky, iridescent, white or slightly yellow crystals, unlike the corresponding arsonium iodides, separate out. They are decomposed by moisture and give off a cacodyl odor, but are stable in dry air. No analysis of these compounds has yet been made. On theoretical grounds, they are more likely to be of the type R₂AsH.HI than R₃As.HI, one of which they undoubtedly must be. From the above review it is seen that the amines, phosphines and arsines show closer analogies in their reactions with alkyl halides than with any other reagent.

When the primary¹ and secondary² aliphatic amines are heated with carbon bisulphide in alcoholic solution, alkyl and dialkyl dithiocarbamic acids are formed. For instance :



and



The tertiary aliphatic amines form, with carbon bisulphide, simple addition-products, which are decomposable at ordinary temperatures.³ Tertiary phosphines form analogous stable substances.⁴

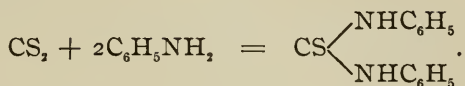
¹ Ber. d. chem. Ges., 1, 25 ; 19, 713 ; 24, 3041 ; Gazz. chim. ital., 24 [II], 281 ; 23 [II], 503 ; This JOURNAL, 22, 24.

² Ber. d. chem. Ges., 14, 2756.

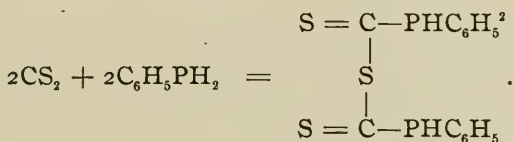
³ *Ibid.*, 33, 13.

⁴ Ann. Chem. (Liebig), Spl., 1, 26, 59 ; Ber. d. chem. Ges., 15, 2017.

Aniline, with carbon bisulphide in alcoholic solution, forms phenylthiourea.¹



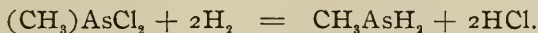
No study has been made of the action of carbon bisulphide on secondary and tertiary aromatic amines, phosphines, or arsines. One primary aromatic phosphine, phenyl phosphine, when heated with carbon bisulphide to 150°, yielded the following :



I have treated ethyl arsine with carbon bisulphide and have obtained triethyl arsine sulphide as the chief product. With phenyl arsine I have obtained light colored crystals, which have not been identified. From a consideration of the above facts it is evident that the action of carbon bisulphide on the amines, phosphines and arsines gives rise to quite varied products.

EXPERIMENTAL.

Cacodyl chloride, in alcoholic solution, was found to be reduced very readily by means of zinc and hydrochloric acid.³ It was therefore supposed that monomethyl arsine chloride would react under the same conditions, according to the equation :



The earlier experiments, though giving positive evidence of the formation of primary arsine, did not yield the substance in the liquid form.⁴ I have since learned that this was largely owing to the quality of the zinc employed. In my most suc-

¹ Ber. d. chem. Ges., 6, 967.

² *Ibid.*, 12, 338.

³ *Ibid.*, 27, 1378.

⁴ *Ibid.*, 34, 3594.

cessful experiments I have used zinc dust amalgamated by treatment with solution of mercuric chloride. In the case of methyl and ethyl arsines, the hydrogen evolved at first is rich in the arsine. When unamalgamated zinc dust is employed the hydrogen evolved may preponderate greatly and the evolved arsine may be less than the quantity necessary to produce its vapor tension at the temperature of the freezing-mixture. In one experiment 150 grams of $\text{MgC}_2\text{H}_5\text{AsO}_3$ were treated with unamalgamated zinc, but not a drop of ethyl arsine was condensed at -10° .

In each of the following experiments which were made to determine the ratio of hydrogen and arsine evolved, 10 grams of zinc dust, 5 grams of $\text{MgC}_2\text{H}_5\text{AsO}_3$, 10 cc. of alcohol, and 10 cc. of concentrated hydrochloric acid were employed; the evolved gases were passed into bent eudiometers and the volumes read. The arsine was then determined by treatment with a silver nitrate solution, the loss in volume representing the arsine itself:

I. Ethyl Arsine Prepared by the Use of Unamalgamated Zinc Dust.

Fractions.	Gas evolved.	Residual gas.	Difference.	Per cent of arsine.
1	41.1	40.8	0.3	0.73
2	48.8	45.4	3.4	7.69
3	45.9	39.6	5.7	12.42
4	48.6	40.6	8.0	16.46
5	50.0	40.7	9.3	18.60
6	47.9	38.2	9.7	20.25
7	44.7	33.2	11.5	25.72
8	48.7	39.0	9.7	19.91
9	. .	. .	. .	. .
10	46.6	38.7	7.9	16.95

II. Ethyl Arsine Prepared by the Use of Amalgamated Zinc Dust.

1	47.2	46.5	0.7	1.48
2	48.0	44.7	3.3	6.90
3	49.2	35.3	13.9	28.16
4	46.7	23.6	23.1	49.46
5	48.9	21.5	27.4	56.03

III. Ethyl Arsine Prepared by the Use of Amalgamated Zinc Dust.

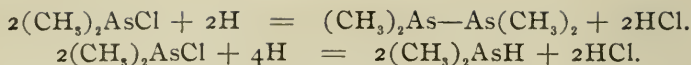
Fractions.	Gas evolved.	Residual gas.	Difference.	Per cent of arsine.
1	49.8	48.3	1.5	3.01
2	49.5	36.6	12.9	26.06
3	51.0	33.0	16.0	31.37
4	48.0	25.8	22.2	46.25
5	44.9	23.1	21.8	48.55
6	43.2	23.6	19.6	45.37
7	19.3	11.5	7.8	40.41

The following percentages of *methyl arsine* were obtained by means of amalgamated zinc dust :

	I.	II.
1	21.5	8.0
2	36.5	19.5
3	20.7	29.0
4	20.1	24.5
5	18.3	20.0
6	14.5	14.0
7	. .	10.4

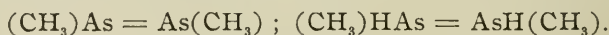
That the percentage of arsine produced does not immediately reach its maximum, is owing to the fact that, at first, the apparatus is filled with hydrogen, which must be displaced by the arsine. From a study of the data of ethyl arsine it is evident that the concentration of arsine, evolved from amalgamated zinc dust, is almost twice that evolved from ordinary zinc dust.

Three years ago, when the problem of primary arsines was suggested to me by A. W. Palmer, the electrolytic reduction of alkylated arsenic derivatives seemed to present a favorable means for obtaining these elusive compounds. The electrolytic reduction of cacodyl chloride was first attempted. The results of quite elaborate experiments, not yet published and not included in this paper, showed the interesting fact that the reduction to the arsine proceeded by two steps. First cacodyl chloride was reduced to nascent cacodyl groups, which either combined to form cacodyl itself, or yielded arsine by union with the nascent hydrogen. These reactions are shown in the following equations :



Twice as much hydrogen is required in the second reaction as in the first. The cacodyl was separated and identified in the early stages of the reduction.

There is considerable evidence that by the reduction of monoalkylated arsenic compounds to primary arsines an analogous intermediate product is formed: (1) when the alcohol is omitted in the reduction of methyl arsonic acid to methyl arsine, an oily substance is produced and rapidly changes to the bright red solid previously mentioned. If alcohol is used, there is no evidence of the formation of any compound other than the arsine. Hence, the reason for the use of alcohol in the preparation of aliphatic primary arsines is evident. (2) During one experiment the reduction of methyl arsonic acid was interrupted at an early stage by pouring out the contents of the flask. The last portion adhering to the zinc, gave rise, spontaneously, to a flame 2-3 feet in height. The combustion-products had the characteristic odor of the arsenic compounds and deposited much metallic arsenic on the surrounding vessels. The oily substance adhering to the zinc could not be methyl arsine because that boils at 2° , nor could it be any of the other known monoalkyl arsenic compounds. It may be one of the following compounds, as yet unknown, analogous to cacodyl:



Monomethyl Arsine.

This arsine is most conveniently prepared in the following manner: Excess of moist zinc dust, amalgamated by means of mercuric chloride, is placed in a flask of considerable capacity. The flask is connected with a wash-bottle, containing water, to remove vapors of hydrochloric acid and alcohol. A long drying tube filled with soda-lime is interposed between the wash-bottle and a condenser of special form.¹

Methyl arsine was always liquefied by means of solid carbon dioxide, though perhaps a good freezing-mixture of pulverized ice and a salt may answer the purpose. The exit tube of the

¹ Ber. d. chem. Ges., 34, 3597.

condenser should be connected with two wash-bottles, the first containing concentrated sulphuric acid and the second concentrated nitric acid. The former excludes moisture and the latter serves the purpose of destroying uncondensed arsine. As methyl arsine, like dimethyl arsine, rapidly destroys rubber, as many of the connections as possible should be made by sealing the glass together. The reaction flask, which may carry a rubber stopper, is supplied with a dropping funnel. A little dilute hydrochloric acid is slowly added until the air in the apparatus is displaced by the evolved hydrogen. A quantity of alcohol, approximately equal to the volume of hydrochloric acid that will be used for the reduction, is then run in. The sodium salt of monomethyl arsonic acid, best prepared by the improved method of Klinger and Kreutz,¹ is used for the reduction. It is dissolved in the smallest possible volume of concentrated hydrochloric acid, and the solution poured from any precipitated sodium chloride into the dropping funnel. This acid solution is run into the evolution flask, which is shaken. Evolution of hydrogen and arsine begins at once; to continue the reduction, the dropping funnel is charged with concentrated hydrochloric acid, tightly stoppered and the stop-cock regulated so that 5-10 drops of acid are admitted per minute. The evolved gases, ascending the stem of the dropping funnel, will force down the acid from its bulb.

The arsine, being cooled in the bulbs of the condenser, collects in the lower one, from which it may be admitted into that between the two lower stop-cocks; by closing the upper of these stop-cocks and then opening the lower one, the arsine will be forced by its own vapor-tension through the capillary adapter, into any convenient form of receiver, held in a freezing-mixture. The capillary of the adapter should be long enough and of a diameter sufficiently small to go to the bottom of the receiver. I have used as receivers bulbs with wide capillaries, or test-tubes constricted near the top. Before drawing off the arsine the adapters and the receivers should be filled with carbon dioxide or hydrogen. While held in the

¹ Ann. Chem. (Liebig), 249, 147.

freezing-mixture the stems of the receivers should be sealed in the flame.

The yield of evolved arsine is quantitative, though the amount condensed varies with the efficiency of the freezing-mixture. Instead of using one large evolution flask it is better to use two or three smaller ones.

The combustion of the liquid was made in a tube charged with a sintered mixture of lead chromate and copper oxide. The combustion for arsenic was made in a tube containing granular zinc oxide.

The capillaries of the bulbs were broken at the proper moment by a stout, brass rod entering the combustion tube and reaching to the point where the bulbs were placed.

I. 0.1085 gram liquid gave 0.0514 gram CO_2 and 0.0601 gram H_2O .

II. 0.1072 gram liquid gave 0.0522 gram CO_2 and 0.0501 gram H_2O .

III. 0.0823 gram liquid gave 0.0397 gram CO_2 and 0.0354 gram H_2O .

I. 0.1154 gram liquid gave 0.1943 gram $\text{Mg}_2\text{As}_2\text{O}_7$.

II. 0.1723 gram liquid gave 0.2918 gram $\text{Mg}_2\text{As}_2\text{O}_7$.

By the Hofmann method :

I. 0.0862 gram liquid gave 20.75 cc. of gas.

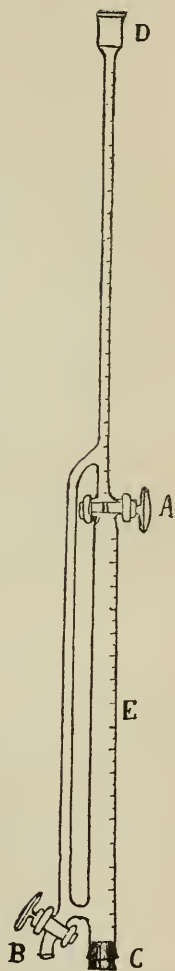
II. 0.0753 gram liquid gave 18.37 cc. of gas.

	I.	II.	III.	Theory.
Carbon	12.92	13.28	13.15	13.09
Hydrogen	6.15	5.19	4.61	5.43
Arsenic	81.46	81.94	. .	81.53
Mol. w't	93.76	91.72	. .	92.00

Monomethyl arsine is a colorless, transparent, mobile liquid, of high refractive power. It is soluble in alcohol, ether, and carbon bisulphide in all proportions. It has a peculiar, very disagreeable and penetrating odor, somewhat resembling that of cacodyl. If breathed even in small quantities it produces, at once, the symptoms of arsenical poisoning. A rat placed in a bottle and caused to breathe the vapors from one drop of the arsine died almost immediately.

The boiling-point was determined in the special apparatus

shown, the tubes of which were graduated in millimeters. The bulb containing arsine, with its moderately long capillary projecting upward, is placed in the lower large tube. With the stopper C and the stop-cocks A and B closed, pure mercury is introduced through the funnel D. A is opened occasionally to allow the mercury to ascend the large lower tube E. As this becomes filled, the capillary of the bulb passes through the hole of the open stop-cock A. More mercury is added until all air is excluded to a point 5 to 10 cm. above the stop-cock A. The apparatus is then placed in a tall cylinder containing a freezing-mixture and permitted to cool. When the temperature of the system is constant the stop-cock A is turned vigorously, so as to break the capillary. The liquid in the bulb begins at once to distil through the stump of the capillary and to depress the mercury. When the mercury has become stationary the temperature and the difference in height of the mercury columns are read. These data, with the barometric pressure, are sufficient to determine the boiling-point. In determining the boiling-point for pressures greater or less than that of the atmosphere, the mercury in the tube open to the air is respectively higher and lower than the level in the large tube E. Monomethyl arsine boils at 2° , under 755 mm. and at 17° , under 1.5 atmospheres pressure.



Solubility in Water.—Primary arsine reacts with a solution of free iodine, according to the following equation. (For evidence see ethyl arsine below.)

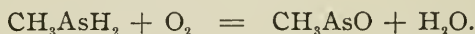


By passing the arsine evolved from the zinc and acid through pure water, treating a measured volume of this solution with

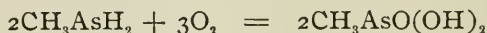
excess of standard solution of iodine in potassium iodide, and finally titrating the excess of iodine by means of a thiosulphate solution, all of the data necessary for the calculation of the solubility in water are easily obtained. Methyl arsine is soluble only to the extent of 85 parts in 1,000,000.

Reactions with Oxygen.

When gaseous methyl arsine is treated, over mercury, with a measured quantity of pure dry oxygen immediate condensation takes place with the separation of a white solid. Readings made immediately gave a decrease in volume approximately equal to twice the volume of arsine used. The following equation expresses the condensation of one volume of the arsine with one volume of oxygen to form the solid methyl arsine oxide (m. p. 95°) :



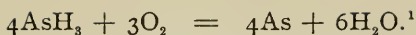
At the end of two weeks the decrease in volume was equal to 2.414 times the volume of the arsine used, or 1.414 volumes of oxygen had condensed with the one volume of arsine. The equation



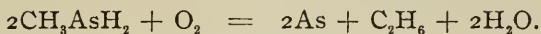
expresses this phenomena. Here 2 volumes of the arsine condense with 3 volumes of oxygen, or 1:1.5, which is approximately equal to the experimental ratio.

Evidence that the latter reaction was according to the second equation is as follows: The final product reacted strongly acid and agreed with the other known properties of methyl arsonic acid. Furthermore, in another experiment, by extracting the water formed by the first reaction with solid calcium chloride, the oxidation did not proceed to the final stage, though the tube was permitted to stand for a number of days.

In one experiment, upon adding the oxygen to the arsine, there resulted a mild explosion, attended by light and the separation of all the arsenic in the metallic form. Analogy for this is seen in the heating of arsine in an insufficiency of oxygen. Here the reaction is largely as follows :

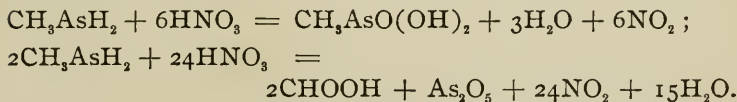


Probably the above reaction of methyl arsine was analogous :



Oxidation by Nitric Acid.

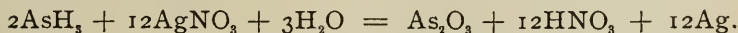
Colored oxides of nitrogen and white fumes were given off and soon small crystals separated when methyl arsine, evolved from the generator, was passed through bulbs containing concentrated nitric acid. When the nitric acid was completely decolorized the contents of the bulbs were removed. The white crystals were filtered off and identified as inorganic arsenic acid. The filtrate was evaporated to dryness, taken up with a little water and permitted to stand for a number of days, when beautiful transparent tablets separated. Through its acid properties, its reduction to products possessing the odor of methyl arsine and the formation of methyl arsine disulphide by reaction with hydrogen sulphide, it was identified as methyl arsonic acid.² A part of the above nitric acid oxidation-product was first treated with sulphuric acid and then with alcohol. Upon fractionating, ethyl formate was found in the distillate. Evidently the reactions of nitric acid on methyl arsine were as follows :



Oxidation by Silver Nitrate.

When methyl arsine is passed into a neutral or an alkaline solution of silver nitrate, immediate precipitation of finely divided metallic silver takes place.

According to Lassaigue³ arsine itself, under these conditions, reacts as follows :



This was disputed, however, by Marchlewski.⁴ I have been

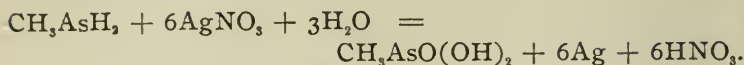
¹ J. prakt. Chem., 6, 347.

² Ann. Chem. (Liebig), 107, 289; 249, 149.

³ Jour. chim. Med., 16, 685.

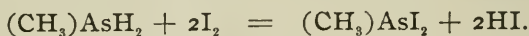
⁴ Ber. d. chem. Ges., 24, 2269.

able to prove the presence of methyl arsonic acid in the reaction-products, so, perhaps, the action is :



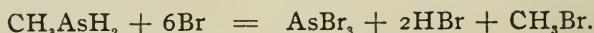
Reactions with Halogens.

Decolorization takes place if the gas from the generator is passed through a solution of iodine in absolute alcohol ; if the solution is treated with only a sufficient amount of the arsine to decolorize and is then evaporated to dryness, amber needles separate. They agreed in properties with those of methyl arsine diiodide ;¹ therefore the reaction was as follows :

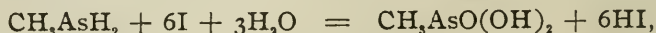


Passing excess of the arsine into the iodine solution resulted in the precipitation of a brown, amorphous mass, which was not identified.

When the gas was passed through a solution of bromine in carbon bisulphide, decolorization took place ; during the passage of arsine heavy white fumes were given off, and towards the end of the experiment the fumes of hydrobromic acid were noticed. The carbon bisulphide was distilled off and left a heavy oil boiling at 220° which was identified as arsenic tribromide,



A bulb containing 0.0541 gram of methyl arsine was broken in a stoppered bottle with excess of standard solution of iodine. After shaking thoroughly, the residual iodine was determined by titrating with sodium thiosulphate ; it was found that 394.88 cc. of iodine solution were required by the methyl arsine. Therefore the reaction proceeded quantitatively according to the equation :



which requires 393.07 cc. of the iodine solution.

Methyl Arsine and Hydrochloric Acid.

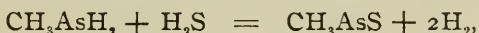
When 11.8 cc. of pure methyl arsine vapor were treated, over

¹ Ann. Chem. (Liebig), 107, 285 ; 249, 152.

mercury, in a graduated tube, with 40.22 cc. of pure, dry hydrochloric acid gas, the resulting volume remained nearly equal to their sum. At the end of two weeks a contraction in volume of 2 cc. was observed; the mixture of gases remaining was treated with solid potash, when the volume of gas decreased to 10.6, a little less than the original volume of the arsine. Upon applying a match to this residual gas, it inflamed and deposited metallic arsenic, indicating that it was unchanged arsine. This experiment shows that if the hydrochloric acid salt of methyl arsine was formed at the ordinary temperature and pressure, it was produced only in small proportion.

Methyl Arsine and Hydrogen Sulphide.

When 17.4 cc. of pure methyl arsine vapor were treated as above with 53.67 cc. of pure dry hydrogen sulphide gas (total 71.07 cc.), the volume, after four days, was 71.61 cc. After remaining for eight weeks in contact with solid potash, the residual gas measured 18.75 cc., or 1.34 cc. more than the original volume of the arsine. If the reaction were as follows:



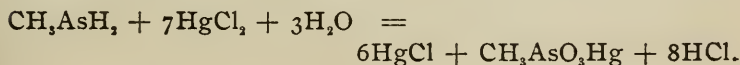
it was only partial.

Methyl Arsine and Phosphorus.

A piece of yellow phosphorus was permitted to stand in contact with a known volume of pure methyl arsine vapor. No change was observed in the volume even after a number of days at ordinary temperature, and after having been heated at 100°.

Methyl Arsine and Mercuric Chloride.

Methyl arsine, passed into aqueous solution of mercuric chloride, separated a white, finely divided precipitate. Upon filtering, washing and treating it with ammonia, a blackening showed the presence of mercurous chloride. Therefore the reaction was probably as follows:



Methyl Arsine and Alkyl Iodides.

a. 8.69 cc. of methyl arsine were treated with 33.26 cc. of methyl iodide vapor (total 40.97 cc.). After eight hours the volume was 40.25 cc., and after eight weeks 18.83 cc. A yellow, crystalline solid began to form immediately on the walls of the tube and continued to increase during a number of days.

b. 7.24 cc. of methyl arsine were treated with 37.3 cc. of methyl iodide vapor (total 44.54 cc.). After two weeks the volume was found to be 18.09 cc., or the mixture of vapors had suffered a contraction in volume of three to four times the volume of the arsine used. The residual gas was treated with solid potassium hydroxide, which gave, on withdrawal, good tests for iodine. The yellow solid formed was found to melt with decomposition at 100° – 102° .

c. A bulb of methyl arsine and excess of methyl iodide were sealed in a large tube. The arsine bulb was broken by agitating the contents of the tube. The methyl iodide, at first slightly colored by iodine, was decolorized immediately. After a few hours yellow crystals began to separate; when the tube was opened no pressure was observed. Upon distilling off the excess of methyl iodide, a heavy yellow oil and a number of crystals were found, both of which dissolved in water with evident decomposition. These crystals can be formed by passing methyl arsine, from a generator, through Geissler bulbs containing methyl iodide.

As was stated above, when primary arsines are heated with halides of hydrocarbons, particularly with alkyl iodides, arsonium compounds are formed. The best method for their preparation is as follows:

The arsine is sealed in bulbs, or better, in convenient-sized test-tubes. Excess of the alkyl halide is also sealed in bulbs or test-tubes. The arsine and the alkyl halide, together with a heavy glass rod, are placed in a convenient-sized sealing tube. After the end of the sealing tube has been constricted in the flame the air in the tube is replaced by carbon dioxide and the tube is immediately sealed. When cold, the contents of the tube are agitated until the bulbs or test-tubes are broken.

The reaction is complete, after heating from six to eight hours at 100° – 150° . The contents of the tube are always colored red by a little arsonium periodide and only a little pressure is developed.

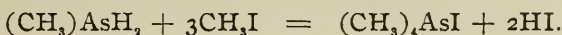
Tetramethyl Arsonium Iodide.

Methyl arsine was heated with excess of methyl iodide in a sealed tube for eight hours at 110° . The colored liquid was washed with benzene. The lower layer was removed, decolorized by means of potassium hydroxide and extracted with chloroform. The solution was dried by calcium chloride and concentrated on the water-bath. The crystals separating were washed with a little benzene and were found to be tetramethyl arsonium iodide.¹

0.1201 gram substance gave 0.1075 gram AgI.

	Theory.	Found.
I	48.67	48.55

The reaction under the above conditions was



Methyl Triethyl Arsonium Iodide.

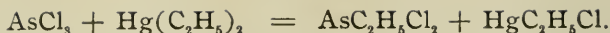
About 1 gram of methyl arsine was heated for eight hours, at 110° , with 6 grams of ethyl iodide; before heating, a number of the crystals mentioned above were noticed. They were nearly white and were well-defined needles. After heating, the red oil was treated as above. On evaporating on the water-bath globules of the arsonium iodide separated and on cooling formed white crystals.

Homologues of Methyl Arsine.

On account of the low boiling-point of methyl arsine, difficulties in condensing and handling it were met with. To avoid these I undertook experiments to prepare the higher boiling ethyl compound. The only method available for the preparation of the initial substance $\text{C}_2\text{H}_5\text{AsO}_3\text{Na}_2$, was that of La Coste.² He treated arsenic trichloride with mercury ethide, and found them to react as follows:

¹ Ann. Chem. (Liebig), 92, 361; 116, 364; 122, 192. Z. physik. Chem., 13, 301.

² Ann. Chem. (Liebig), 208, 33.



The ethyl arsine dichloride was digested on the water-bath with dilute nitric acid until the odor of the chloride had disappeared. The solution was then neutralized with potassium carbonate and evaporated to dryness. Upon extracting the residue with absolute alcohol, potassium ethyl arsonate was taken up, while potassium nitrate and potassium arsenate, always present in the reaction-products, were left largely undissolved. Theoretically simple, this method was found to be beset with great experimental difficulties. Mercury ethide is strongly poisonous and could be prepared only with unsatisfactory yields. Arsenic trichloride is itself a dangerous compound and acts best on mercury ethide in excess, giving ethyl arsine dichloride, which is more disagreeable to deal with than the other two substances. It is described by La Coste as follows :¹

“Eine farblose, bei 156° siedende Flüssigkeit von schwachem, etwas van Obst erinnerndem Geruch; es reizt die Schleimhäute der Augen und Nasen sehr heftig, bringt auf der Haut schmerzhaftes Brandblasen hervor, und ist für den Arbeiter sehr gefährlich da seine Dämpfe Athemnoth, Ohnmacht und lange andauernde Lähmung und Gefühlslosigkeit der Extremitäten bewirken.”

For these reasons the preparation of ethyl arsine dichloride was triply disagreeable and dangerous. Furthermore, it was found to be impossible to fractionate it from the excess of arsenic trichloride and on account of the easy volatility of ethyl arsenic acid, the yields of the latter were found to be insignificant and always contaminated with arsenic acid.

Despairing of La Coste's method for the preparation of ethyl arsonic acid in quantities sufficient for my purpose, that of G. Meyer offered some encouragement.² He had prepared methyl arsonic acid by the action of methyl iodide on sodium arsenite. The only reference to the homologous ethyl body was as follows : “Versuche welche ich im Winter mit Jodäthyl und Arsenit ausstellte zeigten wohl auch die Bildung:

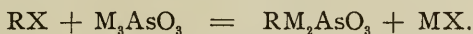
¹ Ann. Chem. (Liebig), 208, 34.

² Ber. d. chem. Ges., 16, 1440.

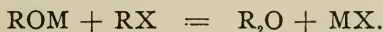
von Aethyl arsinsäure doch bin ich damals, wie mir scheint, nicht zu reinen Producten gelangt."¹

I undertook the preparation of the ethyl compound in the manner that the methyl compound was prepared (Klinger and Kreutz),² but none of the substance sought separated from the alcoholic solution. This I have found to be owing to its ready solubility in both alcohol and water. I have been able, finally, to purify the products of the Meyer reaction, and have developed the method so that it far surpasses that of La Coste in points of elegance, safety and yield.

When alkyl halides in general are treated with alkali arsenites, in a solution made homogeneous by the addition of alcohol, the reaction takes place according to the following general equation :



A secondary reaction also occurs. The alcoholic alkali, always present in the mixture, reacts with the alkyl halides and gives rise to simple ethers :



Unchanged arsenite is always found in the reaction-products. A state of equilibrium is produced when all the alkyl halide is converted into ether and mono-alkyl arsonic acid. The excess of arsenite reduces a little of the alkyl arsonic acid to primary arsine, or its derivatives, imparting to the reaction-product a characteristic, disagreeable odor.

When, for instance, ethyl iodide and potassium arsenite are used, there will be found in the reaction-products, water, alcohol, ether, an arsine derivative, potassium iodide, potassium arsenite, potassium arsenate and potassium ethyl arsonate. The ether, alcohol and arsine derivative can be removed by distilling. If chlorine is passed into the residual aqueous solution, which has been neutralized with hydrochloric acid, all the arsenite is oxidized to arsenate, and the potassium iodide is converted into potassium chloride and free iodine. After the iodine is filtered off and the filtrate treated with magnesia

¹ Ber. d. chem. Ges., 16, 1442.

² Ann. Chem. (Liebig), 249, 147.

mixture, all the arsenic acid is precipitated, while the ethyl arsonic acid remains in solution. Upon boiling the filtrate, magnesium ethyl arsonate precipitates and can be obtained pure by washing with cold water.

Methyl arsonic acid can be prepared by this method, but owing to its difficult solubility in 50 per cent alcohol, it is best prepared by Klinger and Kreutz's modification of Meyer's method.¹ A discussion of the general application of Meyer's reaction and my modification of it is given further on.

Preparation of Magnesium Ethyl Arsonate.

Dissolve completely 318 grams of arsenic trioxide and 540 grams of potassium hydroxide in sufficient water, mix, dilute the solution of potassium arsenite with water to 3 liters and treat with 500 grams of ethyl iodide (1 mol. of ethyl iodide to 1 mol. of potassium arsenite). Sufficient alcohol is now added to produce a homogeneous solution. The mixture is permitted to stand in tightly corked bottles for a number of days, though the reaction is practically complete after a few hours. The solution, which smells strongly of an ethyl arsine derivative, is distilled directly. When all the alcohol is removed the residual aqueous solution is acidified with dilute hydrochloric acid. The white precipitate, consisting essentially of arsenic trioxide and potassium iodide (*vide*, p. 141), is filtered off. A rapid stream of chlorine is now passed into the solution until the dark color, formed by the precipitation of iodine, begins to clear. An excess of chlorine forms the trichloride with the free iodine, this should be avoided, otherwise iodine is precipitated when the filtrate is made ammoniacal.

The iodine is filtered off and the filtrate rendered alkaline with ammonia, it is treated with a large excess of magnesia mixture and permitted to stand at least twenty-four hours. The ammonium magnesium arsenate precipitate is removed by filtration and the filtrate boiled in evaporating dishes. After the ammonia is largely driven off, pure white, small, ball-like masses of magnesium ethyl arsonate separate from the bottom and float. They are filtered and washed with cold water until.

¹ Ann. Chem. (Liebig), 249, 147.

the filtrate gives no test for chlorine with silver nitrate. Pure magnesium ethyl arsonate, containing a variable quantity of water of crystallization, is obtained. The filtrate from the magnesium ethyl arsonate should be treated with more magnesia mixture and boiled to insure complete precipitation of the magnesium ethyl arsonate. Yield 40-50 per cent.

Dried at 140° , the magnesium ethyl arsonate is a pure white, powdery substance, readily soluble in acids but insoluble in alkalies. If it be dissolved in hydrochloric acid and the solution be made ammoniacal, reprecipitation takes place only after boiling. At 22° , 2.31 grams dissolve in 1000 grams of water and 2.66 grams dissolve in 1000 grams of 10 per cent solution of ammonium chloride. At 25° only $\frac{1}{3}$ gram dissolves in 1 liter of ordinary alcohol. As precipitated above, the salt contains varying amounts of water, which most frequently are equal to 1 molecule of water of crystallization.

	Per cent.
Theory Mg in $\text{Mg}(\text{C}_2\text{H}_5)\text{AsO}_3$	13.63
“ “ “ $\text{Mg}(\text{C}_2\text{H}_5)\text{AsO}_3 \cdot \text{H}_2\text{O}$	12.37
“ “ “ $\text{Mg}(\text{C}_2\text{H}_5)\text{AsO}_3 \cdot 3\text{H}_2\text{O}$	10.43

	Per cent.
1. 0.8142 gram substance, dried at 145° , gave 0.5006 gram $\text{Mg}_2\text{P}_2\text{O}_7$	13.29
2. 0.5904 gram substance, dried at 140° , gave 0.3793 gram MgSO_4	12.84
3. 1.2978 grams substance, dried at 25° , gave 0.6824 gram MgSO_4	10.51
4. 0.7677 gram substance, dried at 170° , gave 0.5048 gram $\text{Mg}_2\text{P}_2\text{O}_7$	14.58

It is evident that heating to a temperature as high as 170° produces partial decomposition, while 145° is not high enough to cause complete dehydration. The anhydrous magnesium salt, on ignition, yields water, magnesium oxide, metallic arsenic and a hydrocarbon which burned with a light yellow flame, gave no deposit of arsenic by the Marsh test and did not readily decolorize bromine water.

Ethyl Arsine Disulphide.

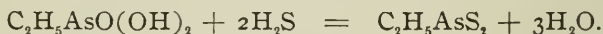
When hydrogen sulphide is passed through a hydrochloric

acid solution of magnesium ethyl arsonate, a heavy yellow oil separates slowly. (This separation is so slow that ethyl arsonic acid may be freed from arsenious acid by fractional precipitation.) When decanted free from the aqueous solution, washed with distilled water, dried by means of calcium chloride and filtered through a dry filter kept warm, it is obtained pure.

0.134 gram substance gave, by the Carius method, 0.1856 gram BaSO_4 .

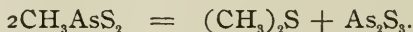
	Calculated for $\text{C}_2\text{H}_5\text{AsS}_2$.	Found.
S	38.09	38.04

The reaction was, therefore, as follows :



The disulphide is a highly viscid, light yellow oil of a peculiar, very disagreeable odor. At 24° its specific gravity is 1.836. It is insoluble in water, alcohol and ether, sparingly soluble in ligroin and easily soluble in benzene, chloroform and carbon bisulphide. Like As_2S_3 , CH_3AsS_2 ¹ and $\text{C}_6\text{H}_5\text{AsS}$,² it is insoluble in concentrated hydrochloric acid. It is very soluble in alkalis and alkali sulphides, from solutions in which it is reprecipitated by acids. It is easily dissolved by dilute nitric acid, forming ethyl arsonic acid. Concentrated nitric acid acts on it with explosive violence yielding the oxidation products ethyl arsonic acid, acetic acid and inorganic arsenic acid.

According to G. Meyer³ and Klinger and Kreutz,⁴ upon heating methyl arsine disulphide the decomposition is as follows :



Meyer stated that the reaction was perfectly analogous to Baeyer's decomposition of methyl arsine tetrachloride :⁵



The only evidence advanced that methyl sulphide was one of the products and that the reaction proceeded as above, was

¹ Ber. d. chem. Ges., **16**, 1440; Ann. Chem. (Liebig), **249**, 153.

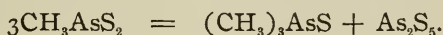
² Ber. d. chem. Ges., **15**, 1955.

³ *Ibid.*, **16**, 1441.

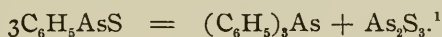
⁴ Ann. Chem. (Liebig), **249**, 154.

⁵ *Ibid.*, **107**, 274.

the strong odor of the methyl sulphide. I have not been able to prove the formation of methyl sulphide in the decomposition products of methyl arsine disulphide, but I have found another compound, the odor of which may have been confused with that of methyl sulphide. It is trimethyl arsine sulphide, and the equation representing the decomposition of methyl arsine disulphide is as follows :



A somewhat analogous reaction is the following :



Trimethyl arsine sulphide is a solid which crystallizes in tough, glistening, white needles and melts at 174° . The analogous ethyl body has been studied carefully because it is also formed upon heating ethyl arsine and carbon bisulphide in alcoholic solution (*vide*, p. 147).

Triethyl Arsine Sulphide.

When ethyl arsine disulphide is heated in a bath at 195° , darkening of the liquid takes place, the light yellow color being changed to a red amber. Triethyl arsine sublimes in the form of beautiful white needles which are conveniently collected in the following manner: A round bottom flask containing the ethyl arsine disulphide is heated in a bath at 180° – 195° ; if the temperature is too high, secondary decomposition takes place. A colorless oil, with a strong cacodyl odor, is formed. Test-tubes of a size large enough to fit closely are filled with cold water and inserted in the neck of the flask. In a short time drops of melted triethyl arsine sulphide, or its crystals, are deposited upon the test-tube. It is withdrawn and placed in a beaker containing carbon bisulphide to dissolve off the deposit, while another test-tube is inserted. When no more crystals are formed upon the test-tubes, the carbon bisulphide solution is concentrated. White needles separate. After filtering and washing with carbon bisulphide, they are obtained pure.

¹ Ber. d. chem. Ges., 15, 1957.

I. 0.2636 gram substance gave 0.3629 gram CO_2 and 0.1783 gram H_2O .

II. 0.27 gram substance gave 0.367 gram CO_2 and 0.1866 gram H_2O .

III. 0.147 gram substance gave 0.1771 gram BaSO_4 .

	Calculated for $(\text{C}_2\text{H}_5)_3\text{AsS}$.	I.	Found.	II.
C	37.11	37.54		37.07
H	7.73	7.58		7.68
S	16.49	16.55		. .

Landolt¹ obtained this compound by digesting triethyl arsine with sulphur. He gave the melting-point as somewhat over 100° . I find that it melts sharply at 119.5° . He describes the compound as odorless when pure. Though I have prepared the compound in a state purer than Landolt's, as shown by the analytical data, I find that it still possesses a very peculiar, penetrating and disagreeable odor. In its other properties it agrees with Landolt's compound. Treated with concentrated hydrobromic acid the following reaction took place:



The hydrogen sulphide given off was easily detected by moist lead acetate paper. The residue was concentrated on the water-bath and the crystals separating were dried on a clay plate and recrystallized from chloroform. Thus obtained they were nearly pure white needles.

0.0412 gram substance gave 0.0716 gram AgBr .

	Calculated for $(\text{C}_2\text{H}_5)_3\text{AsBr}_2$.	Found.
Br	49.69	48.96

Magnesium Methyl Arsonate.

This salt can be prepared in a manner analogous to the ethyl salt described above, or by treating a solution of the sodium salt, prepared by the method of Klinger and Kreutz,² with magnesia mixture and boiling it. By using potassium arsenite instead of sodium arsenite and proceeding as above, a

¹ Ann. Chem. (Liebig), 89, 326.

² *Ibid.*, 249, 149.

somewhat better yield of the methyl salt can be obtained than by Klinger and Kreutz's method. When methyl arsonic acid is desired in a short time, the method given above is more practical, but more laborious than that of Klinger and Kreutz.

Magnesium methyl arsonate, unlike the ethyl salt, is partially precipitated in the cold on adding magnesia mixture to a solution of its salt. Small white crystals, of a more homogeneous composition than that of the analogous ethyl salt, are obtained. They are readily soluble in acids, from which solutions ammonia, in excess, reprecipitates the magnesium salt without boiling, though not completely.

I. 0.8027 gram substance, dried in desiccator five days, gave 0.3505 gram $\text{Mg}_2\text{P}_2\text{O}_7$.

II. 0.6543 gram substance, dried in desiccator five days, gave 0.2859 gram $\text{Mg}_2\text{P}_2\text{O}_7$.

	Calculated for $\text{MgCH}_3\text{AsO}_3 \cdot 5\text{H}_2\text{O}$.	I.	Found.	II.
Mg	9.52	9.44		9.45

The salt is soluble, 2.118 grams in a liter of water at 22° and 3.085 grams at 99°

Magnesium Phenyl Arsonate.

A solution of phenyl arsonic acid, treated with magnesia mixture, precipitated $\text{MgC}_6\text{H}_5\text{AsO}_3$ only on boiling.

Silver Phenyl Arsonate.

The salt was prepared and analyzed for the purpose of identifying the oxidation-products of phenyl arsine. It was made by dissolving pure phenyl arsonic acid in ammonia, adding a solution of silver nitrate and then neutralizing with nitric acid. A pure white, glistening, micro-crystalline precipitate was formed. It is practically insoluble in water, as proved by the fact that water, in contact with it, produced scarcely any opalescence with hydrochloric acid. The salt darkens in light.

0.5731 gram salt gave 0.3940 gram AgCl .

	Calculated for $\text{Ag}_2\text{C}_6\text{H}_5\text{AsO}_3$.	Found.
Ag	51.90	51.78

As methyl, ethyl and phenyl arsonic acids are precipitated by the magnesia mixture only on boiling, a general means is available for the separation of organic arsenic acids from the inorganic ones. It is to be expected that propyl arsonic acid and its homologues, and phenyl arsonic acid and its homologues, if prepared by G. Meyer's reaction,¹ could be separated and purified by the method indicated above. That they are formed by Meyer's reaction may be seen by the following experiments :

G. Meyer's Reaction.

The object of the experiments described below was to determine the best conditions for Meyer's reaction and the extent of its applicability. The alkali arsenites were treated with the alkyl halides in sufficient water and alcohol to insure homogeneous solutions. After standing at ordinary temperatures, or heating in sealed tubes, the solutions were evaporated to dryness on the water-bath. The residues were dissolved in water, feebly acidified with dilute sulphuric acid and made alkaline with sodium bicarbonate. The solution was then titrated with iodine solution to determine the unchanged arsenite. The alkyl arsonic acids, containing pentavalent arsenic, are not affected by free iodine. The difference between the amount of arsenite used and the amount found by titration, represents the amount fixed by the organic groups. A ready means is thus afforded for determining the yields in the Meyer reaction.

I. Ethyl iodide and Na_3AsO_3 (1 mol. to 1 mol.) :

- | | | | | | | | | | | |
|----|-------|-----|-------|---------|-------|-----|------|-------|---------|-------|
| 1. | After | 24 | hours | yielded | 43.76 | per | cent | ethyl | arsonic | acid. |
| 2. | " | 72 | " | " | 40.17 | " | " | " | " | " |
| 3. | " | 91 | " | " | 46.36 | " | " | " | " | " |
| 4. | " | 120 | " | " | 42.50 | " | " | " | " | " |

These experiments show that the reaction is complete at the end of twenty-four hours.

¹ Ber. d. chem. Ges., 16, 1440.

II. Ethyl iodide and Na_3AsO_3 (1.5 mols. to 1 mol.):

1.	After	11	hours	yielded	42.77	per cent	ethyl	arsonic	acid.
2.	"	115	"	"	44.35	"	"	"	"
3.	"	115	"	"	43.03	"	"	"	"
4.	"	168	"	"	46.65	"	"	"	"

Here an excess of the alkyl iodine does not seem to be of any advantage.

III. Ethyl iodide and K_3AsO_3 (1 mol. to 1 mol.):

1.	After	1	hour	yielded	63.90	per cent	ethyl	arsonic	acid.
2.	"	16	hours	"	67.65	"	"	"	"
3.	"	48	"	"	70.30	"	"	"	"
4.	"	48	"	"	70.25	"	"	"	"

These experiments show that the yield is nearly doubled by using potassium arsenite instead of sodium arsenite. Also that the reaction is nearly complete in one hour. Much less alcohol was required with potassium arsenite than with sodium arsenite. For these reasons it is of advantage to use potassium arsenite in Meyer's reaction.

IV. Ethyl iodide + K_3AsO_3 (1.5 mols. to 1 mol.):

1.	After	16	hours	yielded	72.75	per cent	ethyl	arsonic	acid.
2.	"	48	"	"	76.00	"	"	"	"

Excess of ethyl iodide in this case produces only a slight increase in the yield.

V. Ethyl bromide and K_3AsO_3 (1 mol. to 1 mol.):

1.	After	5	hours	yielded	11.20	per cent	ethyl	arsonic	acid.
2.	"	24	"	"	22.20	"	"	"	"
3.	"	28	"	"	22.17	"	"	"	"
4.	"	120	"	"	22.62	"	"	"	"

It is evident that the bromide is not so well adapted for alkylation as the iodide. After heating the ethyl bromide with the potassium arsenite in a sealed tube, for six hours, at 110° , the yield was only 9.5 per cent. Here a quantity of alcohol insufficient to produce a homogeneous solution was used.

Other studies are indicated in the following table:

Hydrocarbon substituent.	Time.	Yield.
Ethyl nitrite	48	3.25
Ethylene bromide	20	2.10
“ “	168	11.30
<i>n</i> -Propyl iodide	24	19.80
Isopropyl iodide	48	4.50
Isoamyl “	24	2.41
“ “	50	5.06
“ “	168	20.00
Phenyl “	20	8.30
“ “	48	7.25
“ “	144	7.43
“ bromide	14	8.70
Toluyll iodide	51	8.10
Benzyl “	50	27.88
“ “	69	33.00
“ “	71	33.62

The arsonic acids of *n*-propyl, isoamyl and benzyl iodides would seem to admit of easy preparation. I have experiments in progress to prepare these acids and their corresponding arsines.

These results show that although alkylation continues to take place as the molecular weight of the alkyl haloid increases, yet, in the aliphatic series, the yields are inversely as the molecular weights. Benzyl iodide gives a larger per cent than phenyl iodide because, in its reactions, it is more closely allied with methyl iodide than with phenyl iodide. All the arsonic acids hitherto known are given below :

1	Methyl ¹
2	Ethyl ²
3	Phenyl ³
4	Nitrophenyl ⁴
5	Paranisyl ⁵
6	Orthotoluyll ⁶
7	Paratoluyll ⁷
8	Benztoluyll ⁸
9	α -Naphthyl ⁹

¹ Ann. Chem. (Liebig), 107, 263 ; 249, 149 ; Ber. d. chem. Ges., 16, 1440.

² Ann. Chem. (Liebig), 208, 34.

³ *Ibid.*, 201, 203.

⁴ Ber. d. chem. Ges., 27, 265.

⁵ *Ibid.*, 20, 51.

⁶ Ann. Chem. (Liebig), 201, 255.

⁷ *Ibid.*, 201, 255.

⁸ *Ibid.*, 208, 3.

⁹ Ber. d. chem. Ges., 11, 1503.

It is evident that a large number of acids could be prepared by Meyer's reaction and that, through their reduction, the corresponding primary arsines and their derivatives could be obtained. Studies along these lines are being made in this laboratory.

When the reaction-product of alkyl iodide and potassium arsenite, in alcoholic solution, is neutralized with hydrochloric acid, copious, small, white, glistening crystals, or a powdery mass is precipitated. This substance is also formed if the solution is strongly alcoholic and is permitted to stand for a number of days; its production was noticed by Klinger and Kreutz,¹ from methyl iodide and potassium arsenite in a strongly alcoholic solution. They stated that the precipitate was not potassium methyl arsonate, but the double compound of potassium iodide and arsenic trioxide studied by Rüdorff,² who found, by analysis, the composition :

	Per cent.	
As ₂ O ₃	70.42	2As ₂ O ₃ .KI
K	6.99	
I	22.58	

I have made analyses of various precipitates produced by acidifying the reaction-products of Meyer's reaction and drying to constant weight in desiccators. I weighed the iodine as the silver salt, the potassium as sulphate and determined the arsenic trioxide in the same manner as Rüdorff, by titration with standard iodine solution.

	Samples.	As ₂ O ₃ .	Potassium.	Iodine.	Sum.
I. Ethyl iodide,	1	10.26	38.41	3.69	52.36
K ₃ AsO ₃ , acidified with					
H ₂ SO ₄	2	10.40	38.80	3.50	52.70
First precipitates	3	.	39.10	3.82	. .
II. Same as I. Last pre-					
cipitate	1	66.23	8.49	21.40	96.12
III. Same as I. Precipitated					
in conc. alcohol	1	60.92	12.17	19.20	92.12
IV. Benzyl iodide, same as I,					
H ₂ SO ₄ . First fraction	1	33.80	26.80	10.85	71.45
Same as IV. Middle					
fraction	1	13.18	31.55	7.69	52.42
Same as IV. Last					
fraction	1	8.36	41.67	2.12	52.15

¹ Ann. Chem. (Liebig), **249**, 155.

² Ber. d. chem. Ges., **19**, 2668.

The above data show that the preparations are far from being homogeneous and do not agree at all with Rüdorff's compound. Moreover the presence of carbon in them can easily be proved and the sum of analytical values is less than 100. It is evident, therefore, that an arrangement of values different from Rüdorff's is necessary. Distributing the constituents among KI, K_3AsO_3 , and $K_2C_2H_5AsO_3$, I obtain :

	Per cent.
$K_2C_2H_5AsO_3$	66.82
K_3AsO_3	4.82
KI	24.88
Total per cent	= 96.52

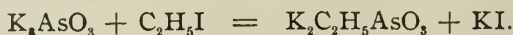
It will be necessary to make direct determinations of the carbon and hydrogen, because the As_2O_3 may be present as such or as K_3AsO_3 . A closer study of these precipitates is required before attempts are made to prepare other arsonic acids by Meyer's reaction.

Ether Formation in Meyer's Reaction.

From the use of 1100 grams of ethyl iodide the following fractions of ordinary ether were separated from the alcoholic reaction solution :

		Grams.
1	below 40°,	40
2	40°-45°,	25
3	45°-55°,	24
4	55°-65°,	10
5	65°-75°,	8
Total,		107

Considering 75 grams of this weight pure ether, it would be equivalent to 315 grams of ethyl iodide, or about 30 per cent of the amount used. Therefore about this per cent of ethyl iodide reacts with sodium ethylate and the remaining 70 per cent with potassium arsenite :



This agrees with the yield of ethyl arsonate as determined above.

Ethyl Arsine,
 $C_2H_5AsH_2$.

Ethyl arsine is easily obtained from magnesium ethyl arsonate, by the method used for the preparation of methyl arsine. A freezing-mixture of salt and ice is employed instead of solid carbon dioxide. The yield is quantitative, though the amount that can be condensed is only about 60 per cent.

If the alcohol is omitted in the reduction of ethyl arsonic acid, a transparent oil, of a cacodyl-like odor, may be seen floating on the surface of the solution. A specimen (0.084 gram), condensed in a sulphur dioxide tube, boiled above 100° , under 481 mm. Apparently it contained ethyl arsine and an intermediate product of reduction (*vide*, p. 120).

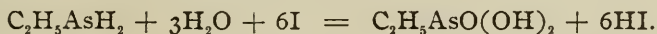
The combustion of the ethyl arsine was conducted in the same manner as that of methyl arsine.

0.0937 gram substance gave 0.0056 gram H_2O and 0.0776 gram CO_2 .

0.1468 gram substance gave 0.2146 gram $Mg_2As_2O_7$.

	Calculated for $C_2H_5AsH_2$.	Found.
C	22.64	22.58
H	6.60	6.64
As	70.75	70.73

Ethyl arsine is a liquid resembling methyl arsine in its physical and chemical properties. It boils at 36° as determined in the apparatus used for methyl arsine; the sp. gr. at 22° is 1.217. Its solubility in water was found to be 126 parts in a million at 19° , the value being obtained by means of the reaction expressed by the equation:

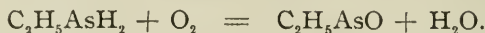


Its odor differs somewhat from that of methyl arsine, but, like the latter, it is extremely disagreeable and penetrating. A rat permitted to breathe a little of its vapor, died almost immediately. Its slow oxidation products with air are colored light yellow, instead of bright red, as in the case of methyl arsine.

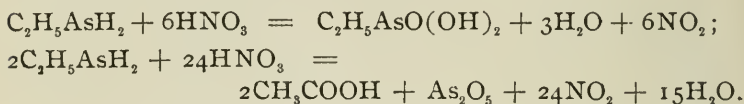
Oxidation of Ethyl Arsine.

When 33.37 cc. of ethyl arsine vapors were treated with

180.20 cc. of dry air, a contraction of 60.71 cc. was shown at the end of twenty-four hours. The reaction was mainly :

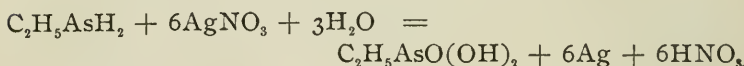


When ethyl arsine from the generator was passed through concentrated nitric acid, brown oxides of nitrogen were given off and inorganic arsenic acid soon separated. The solution was proved to contain ethyl arsonic and acetic acids. The reactions may be expressed as follows :



With silver nitrate, in either neutral or alkaline solution, immediate precipitation of metallic silver takes place; when 25 cc. of water, saturated with ethyl arsine and calculated to contain 0.0043 gram, were treated with excess of ammoniacal silver nitrate, 0.005 gram of metallic silver was obtained.

The equation



requires the precipitation of 0.0261 gram of silver, which is about five times the amount found. Evidently most of the silver remains in solution as the silver salt of ethyl arsonic acid.

Ethyl Arsine and Sulphuric Acid.

Upon passing ethyl arsine through concentrated sulphuric acid and allowing the liquid to remain for a number of days, beautiful white compact crystals separated, which are difficult to obtain free from sulphuric acid. Upon exposure to the air, or by treatment with water, an arsine-like odor was given off. The crystalline compound is evidently a salt of ethyl arsine and sulphuric acid, probably having the composition, $(\text{C}_2\text{H}_5\text{AsH}_2)_2 \cdot \text{H}_2\text{SO}_4$ analogous to $(\text{CH}_3\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4$ and $(\text{C}_2\text{H}_5\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4$.¹ Experiments with the condensation products of primary and secondary arsines, with sulphuric acid,

¹ Ann. Chem. (Liebig), 193, 73.

the halogens and halogen acids, are in progress in this laboratory and tend to establish the basicity of the arsines.

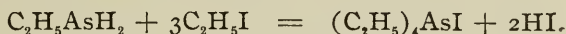
Tetraethyl Arsonium Iodide,
 $(C_2H_5)_4AsI$.¹

Excess of ethyl iodide was heated with 2.89 grams of ethyl arsine, for eight hours, at 110°. The red liquid was washed with benzene, then with a little potassium hydroxide solution to remove the iodine and was finally extracted with chloroform. The solution was dried over calcium chloride, concentrated on the water-bath and treated with a little benzene, when pure white crystals of tetraethyl arsonium iodide separated.

1.1311 grams substance gave 0.835 gram AgI.

	Theory.	Found.
I	39.93	39.90

The reaction was as follows :



Ethyl Trimethyl Arsonium Iodide.

When the bulbs of ethyl arsine and methyl iodine were broken, iridescent, transparent needles were produced which increased in volume on standing and became more compact in form. They were probably the intermediate products mentioned above. The dark red oil was washed with benzene, then treated with concentrated potassium hydroxide. After evaporating on the water-bath a colorless oil separated, from which crystals of ethyl trimethyl arsonium iodide formed on cooling. They were filtered as dry as possible, washed with a little of a mixture of alcohol and ether, dissolved in ordinary alcohol and reprecipitated by means of ether. After filtering, they may be recrystallized from alcohol directly. Beautiful, hard, glistening needles are formed. Ethyl trimethyl arsonium iodide does not melt at 300°; it softens somewhat at this temperature and shrinks considerably at 320°. It is soluble in water, chloroform and hot alcohol; somewhat

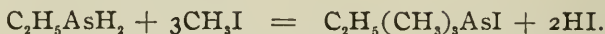
¹ Ann. Chem. (Liebig), 89, 33; 92, 364.

difficultly soluble in cold alcohol or concentrated potassium hydroxide, and insoluble in ether.

0.2275 gram substance gave 0.1945 gram AgI.

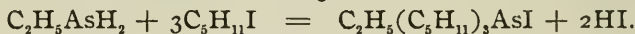
	Calculated for $\text{C}_2\text{H}_5(\text{CH}_3)_3\text{AsI}$.	Found.
I	46.07	46.20

Reaction was as follows :



Ethyl Triisoamyl Arsonium Iodide.

Two grams of ethyl arsine and excess of isoamyl iodide were heated for eight hours at 140° . The red oil was washed with benzene, decolorized and evaporated with concentrated potassium hydroxide solution; the precipitate was filtered, washed with ether and dissolved in hot alcohol. Upon concentrating the alcoholic solution and cooling, compact crystals separated. They were found to be difficultly soluble in chloroform, easily so in isoamyl alcohol and ordinary alcohol and insoluble in ligroin and acetone. Ethyl triisoamyl arsonium iodide does not melt at 250° . Reaction was as follows :



Ethyl Arsine and Carbon Bisulphide.

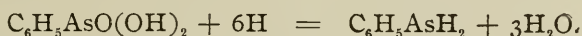
A mixture of 2.0528 grams ethyl arsine, 8.2529 grams carbon bisulphide and 6.5862 grams absolute alcohol was heated in a sealed tube, for ten hours, at 120° . Upon opening the tube no pressure was noticed; after evaporating the excess of carbon bisulphide and alcohol a heavy oil with a peculiar, mustard-like, disagreeable odor remained. Its maximum boiling-point was 220° . The fraction above 200° , on standing for a number of days, deposited long needles, which, being filtered and recrystallized from carbon bisulphide, were found to melt sharply at $119^\circ.5$. This agrees with the melting-point of triethyl arsine sulphide mentioned above. The odor and other properties of the two substances were found to be identical.

The oil which was filtered from the triethyl arsine sulphide had a very irritating cacodyl-like odor. Too little of it was obtained for analysis. At present no equation can be given

that will represent this peculiar reaction. Whether triethyl arsine sulphide is the end product, or results from some intermediate compounds, cannot be stated.

Phenyl Arsine,
 $\text{C}_6\text{H}_5\text{AsH}_2$.

This compound, the analogue of aniline, was prepared from the calcium salt of monophenyl arsonic acid.¹ A quantity of the pure salt was mixed with excess of amalgamated zinc dust, covered with water and then with a layer of ether. The flask was connected with a return condenser, at the top of which was inserted a rubber stopper carrying a dropping funnel and a tube bent down into mercury. The latter permitted the escape of hydrogen without admitting air. Hydrochloric acid was added at the rate of 3-5 drops per minute. After a number of hours the reaction was complete, according to the equation:



This is contrary to the view of La Coste and Michaelis.² "Die Monophenylarsinsäure zeichnet sich in ihrem Verhalten gegen Oxydations- und Reductionsmittel durch ungemeine Beständigkeit aus; — Durch Zink findet weder in alkalischer noch in saurer Lösung eine nennenswerthe Reduction statt; es hört zwar beim Zufügen der Säure zu dem Reductionsgemisch für einige Zeit die Wasserstoffentwicklung auf und gleichzeitig macht sich ein unangenehmer knoblauchartiger Geruch bemerklich, aber auch nach längerer Einwirkung lässt sich der grösste Theil der Säure unverändert wieder abscheiden. Es geschieht diess am einfachsten, indem man die, im Falle eine alkalische Lösung benutzt war, mit Schwefelsäure angesäuerte, etwas erwärmte Flüssigkeit mit Aether ausschüttelt; bei längerem Stehen, oder beim Verdunsten der ätherischen Lösung scheidet sich die Säure in feinen Nadeln ab; eigenthümlich ist, dass dieselbe aus stark saurer Lösung in den Aether übergeht, während sie sich, direct damit behandelt, nur spurenweise in demselben löst." This

¹ Ann. Chem. (Liebig), **201**, 203-209; Ber. d. chem. Ges., **27**, 264.

² Ann. Chem. (Liebig), **201**, 204.

was written in 1880. I quote from Michaelis in 1902.¹ "Primary aromatische Arsine RAsH_2 konnten bis jetzt nicht erhalten werden. Alle Reduktionsversuche führten immer zu den Arsenoverbindungen, die keinen Wasserstoff aufnehmen. Doch wurde häufig bei solchem Versuchen ein eigenthumlich durch dringender Geruch wahrgenommen, der von geringen Mengen eines hierbie gebildeten Arsins herzurühren scheint. Vielleicht werden daher doch noch einmal die Bedingungen zur Darstellung dieser interessanten Körperklasse aufgefunden."

Michaelis undoubtedly obtained phenyl arsine by the reduction of phenyl arsonic acid and other phenyl arsine compounds but did not isolate it. The former reduces to the arsine in either acid or alkaline solution. In his earlier experiments Michaelis evidently recovered his phenyl arsonic acid after he had reduced it to phenyl arsine and it had been permitted to reoxidize in the air to the acid. Arsinobenzene, which appeared to be the end reduction product, is really an intermediate one, or else a subsequent oxidation product of the arsine. In a proper solution arsenobenzene is reduced to phenyl arsine.

When the ether layer in the above reduction is removed, dried with calcium chloride and distilled, it is found to contain phenyl arsine. The distillation is best carried on *in vacuo* in a Brühl apparatus, while dry carbon dioxide is admitted through the capillary entering the distilling-flask. After the distillates have been collected carbon dioxide is permitted to fill the apparatus. The capillaries of bulbs which have been previously filled with carbon dioxide and heated are dipped into the liquid arsine. Care must be exercised to exclude air as completely as possible, because the arsine rapidly oxidizes to arsenobenzene, phenyl arsenic acid and phenyl arsine oxide.

The combustion of phenyl arsine was conducted like that of methyl and ethyl arsine except that the breaking of a bulb in the combustion tube was not necessary.

0.1780 gram substance gave 0.3056 gram CO_2 and 0.0718 gram H_2O .

¹ Ann. Chem. (Liebig), 320, 276.

0.2851 gram substance gave 0.2833 gram $\text{Mg}_2\text{As}_2\text{O}_7$.

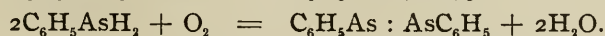
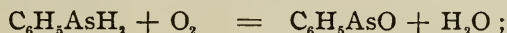
0.1009 gram substance gave, by the V. Meyer method, 18 cc. gas at 31° and 744 mm. pressure.

	Calculated for $\text{C}_6\text{H}_5\text{AsH}_2$.	Found.
C	46.75	46.82
H	4.54	4.43
As	48.70	48.08
Mol. wt.	154.0	150.5

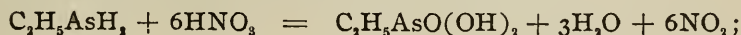
Monophenyl arsine is a transparent, highly refractive, heavy oil boiling at 148° under ordinary pressure, 93° under 70 mm., 84° under 55 mm. and 77° under 33 mm. It is insoluble in water but readily dissolves in alcohol, ether and carbon bisulphide. Its odor, when concentrated, is somewhat like that of phenyl isocyanide, but when dilute it is very pleasant and resembles that of the hyacinth.

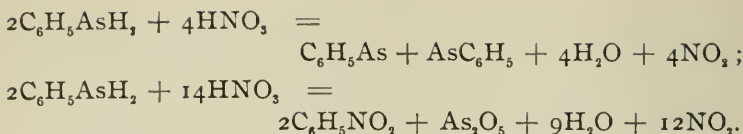
Oxidation of Phenyl Arsine.

In contact with air phenyl arsine rapidly warms and changes into a light yellow, plastic mass. The odor of phenyl arsine oxide is noticeable, while arsenobenzene and phenyl arsonic acid are easily identified in the oxidation-products. Well-formed crystals of arsenobenzene separate if an ethereal solution of phenyl arsine is permitted to oxidize slowly in air; the melting-point agrees with that of arsenobenzene. On evaporating the filtrate, extracting with water and precipitating by means of silver nitrate, in neutral solution, the silver salt of phenyl arsonic acid was formed. The following equations show the oxidations:



Concentrated nitric acid acts on phenyl arsine with explosive violence, an odor of nitrobenzene being evolved. The following equations represent the reactions:





The clear yellow solution resulting was evaporated to remove the excess of nitric acid ; after extracting with chloroform the insoluble residue was identified as arsenobenzene. The chloroform was evaporated and deposited compact crystals. These were washed with a little chloroform, dissolved in ammonia and treated with silver nitrate, in neutral solution. The white silver precipitate was analyzed.

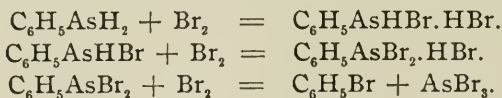
0.4142 gram substance gave 0.2830 gram AgCl.

	Calculated for $\text{Ag}_2\text{C}_6\text{H}_5\text{AsO}_3$.	Found.
Ag	51.92	51.46

The chloroform was shaken up with ammonia, then evaporated on the water-bath and the yellow oil remaining was identified as nitrobenzene. Some of the original solution gave a precipitate in the cold with magnesia mixture. Hence arsenic acid is one of the products of the oxidation. Evidently the energetic action of nitric acid causes a resolution of part of the phenyl arsine according to the third equation above.

Reactions of Phenyl Arsine with Halogens.

With Bromine.—Phenyl arsine was treated with bromine, in ether solution, the liquid decolorized immediately. Excess of bromine was added and the ether distilled off on the water-bath ; a brown-red oil remained, during the distillation, of which fumes of hydrobromic acid were evolved. Bromobenzene was found in the distillate and arsenic tribromide in the residue. The reactions were as follows :



La Coste and Michaelis¹ are authorities for the last equation. That one or the other of the addition-products,

¹ Ann. Chem. (Liebig), 201, 203.

$C_6H_5AsHBr.HBr$ or $C_6H_5AsBr_2.HBr$, was formed during the reaction is indicated by the following experiment :

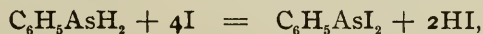
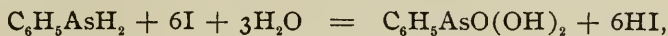
Solution of bromine in anhydrous ether was added, not in excess, to a similar solution of phenyl arsine. A brick-red precipitate was formed, but, hitherto, all attempts to isolate it have failed. It could not be phenyl arsine dibromide, brombenzene, or arsenic tribromide, because all of these are liquids. It might be $C_6H_5AsHBr.HBr$, or $C_6H_5AsBr_2.HBr$, for the following reasons: On exposure to the air it immediately became liquid and evolved hydrobromic acid. That it contains the C_6H_5As group is seen from its decomposition-products yielding phenyl arsine when treated with zinc and hydrochloric acid. Of the two formulas, $C_6H_5AsHBr.HBr$ and $C_6H_5AsBr_2.HBr$, the former is the more probable, for reasons mentioned previously.

With Iodine.—Phenyl arsine immediately decolorizes solution of iodine in potassium iodide. By treating a known weight of the arsine with excess of standard iodine solution, and titrating this excess by means of thiosulphate solution, the following results were obtained :

(1) 0.4227 gram $C_6H_5AsH_2$ took up 1.7032 grams iodine equivalent to 4.8 atoms of iodine.

(2) 0.4819 gram $C_6H_5AsH_2$ took up 1.8853 grams iodine equivalent to 4.7 atoms of iodine.

If the reactions were as follows,



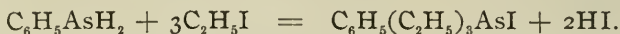
the ratio would be one molecule of the arsine to either 6 or 4 atoms of iodine. The experimental evidence shows that both reactions must take place. Phenyl arsonic acid has been identified among the reaction products.

Reactions with Alkyl Haloids.

*Phenyl Triethyl Arsonium Iodide.*¹—Excess of ethyl iodide was treated with 3.45 grams of phenyl arsine, for six

¹ Ann. Chem. (Liebig), 201, 212.

hours, at 120°. The dark colored oil was washed with benzene, decolorized by means of a solution of caustic potash and extracted with chloroform. The chloroform was evaporated and the iodide which separated was identified by its melting-point, 113°.



Phenyl Trimethyl Arsonium Iodide.

By the use of methyl iodide this substance was prepared in an analogous manner and identified by means of its melting-point, 244°. ¹

Phenyl Triisoamyl Arsonium Iodide.

Three grams of phenyl arsine and 13 grams of isoamyl iodide were heated for six hours at 140°–150°. The product was first extracted with benzene and then with chloroform. The latter solution was dried over calcium chloride and the chloroform evaporated on the water-bath. On cooling, crystals of the arsonium iodide separated which, after washing with ether, were found to be pearly white and to melt at 163°. Phenyl triisoamyl arsonium iodide is very soluble in chloroform and alcohol, but insoluble in benzene, ligroin, ether and cold water.

0.4487 gram substance gave 0.2148 gram AgI.

	Calculated for $\text{C}_6\text{H}_5(\text{C}_5\text{H}_{11})_3\text{AsI}$.	Found.
I	25.81	25.87

Phenyl arsine was heated with excess of phenyl iodide for six hours, at 150°. No arsonium iodide could be separated from the reaction-products. Though tetrabenzyl arsonium iodide² exists, apparently the tetraphenyl arsonium iodide, like the corresponding ammonium and phosphonium compounds, is incapable of formation. Spatial interference perhaps prevents four phenyl groups and an atom of halogen attaching themselves to atoms like nitrogen, phosphorus and arsenic. This interference does not exist in the case of four alkyl or benzyl groups.

¹ Ann. Chem. (Liebig), **207**, 205.

² Centrbl., 1899 (1), p. 890.

The above investigations were carried out under the direction of the late Prof. A. W. Palmer. I wish to express here my sincere thanks for his encouragement and advice given during these researches, which were fraught with many experimental difficulties.

URBANA, ILL.,
October 10, 1904.

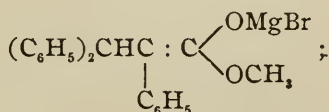
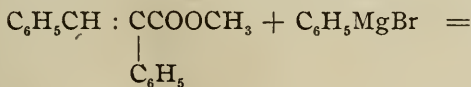
THE REACTION BETWEEN UNSATURATED COMPOUNDS AND ORGANIC MAGNESIUM COMPOUNDS.

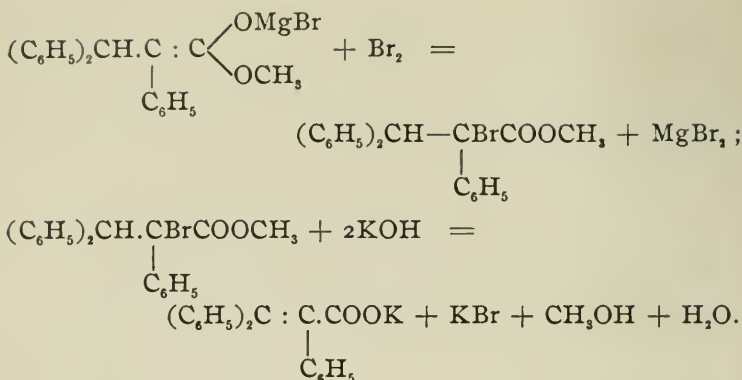
IV. REACTIONS WITH ESTERS OF α -PHENYLCINNAMIC ACID.

BY E. P. KOHLER AND GERTRUDE HERITAGE.

Methyl phenylcinnamate is the first of the unsaturated esters, that have heretofore been studied, to give perfectly clean reactions with organic magnesium derivatives. The nature of the reaction, however, differs with different classes of magnesium compounds. With the substances obtained by dissolving magnesium in aromatic haloids it always consists, exclusively, in 1,4-addition of the organic magnesium compound to the unsaturated ester. The resulting addition-products are crystalline and can be purified by recrystallization from benzene or ether. The substance obtained from phenylmagnesium bromide was isolated in pure condition and analyzed. Unlike the magnesium compounds that are obtained from halogen alkyls, it does not crystallize with a molecule of ether.

This reaction can be used to advantage in the preparation of certain types of unsaturated acids, as is shown by the ease with which triphenylacrylic acid was obtained from phenylcinnamic acid. The successive steps in the process are illustrated by the following equations :





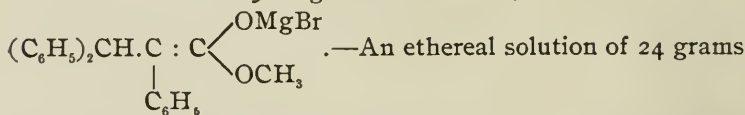
As it is not necessary to purify any of the intermediate products, all of these reactions can be carried out in a single morning. The yield is good—25 grams of pure triphenylacrylic acid from 24 grams of the methyl α -phenylcinnamate.

The esters obtained by using aromatic magnesium compounds, other than phenyl derivatives, contain two dissimilar asymmetric carbon atoms. They should, therefore, be capable of existing in two inactive stereoisomeric modifications. Two isomeric esters were obtained with α -naphthylmagnesium bromide, but as they gave the same acid on hydrolysis, it has not been possible, thus far, to prove that they represent two racemic modifications.

With methylmagnesium iodide α -phenylcinnamic ester reacts like the esters of saturated acids and gives a tertiary alcohol, thus resembling all other unsaturated esters that have been studied.

EXPERIMENTAL.

Reaction with Phenylmagnesium Bromide,



of the methyl ester was added gradually to a boiling solution of 2.5 grams of magnesium, in a mixture of brombenzene and absolute ether. A crystalline magnesium compound began to

separate before one-third of the ester had been added. After addition of the ester the mixture was boiled for half an hour longer and the liquid removed by inverse filtration. The crystalline magnesium compound remaining in the flask was washed with absolute ether and benzene, then redissolved in a large quantity of boiling ether. From this solution it crystallized, on cooling, in small, lustrous prisms. An analysis gave the following results :

0.2501 gram substance gave 0.5748 gram CO_2 , 0.1080 gram H_2O and 0.0240 gram MgO .

	Calculated for $\text{C}_{22}\text{H}_{19}\text{O}_2\text{MgBr}$.	Found.
C	62.94	62.71
H	4.53	4.80
Mg	5.81	5.70

Methyl Triphenylpropionate, $(\text{C}_6\text{H}_5)_2\text{CHCHCO}_2\text{CH}_3$.—In the
 $\begin{array}{c} | \\ \text{C}_6\text{H}_5 \end{array}$

air the clear crystals of the magnesium compound, described above, soon become opaque and in the course of a day the entire mass changed into a thick paste. From this, chloroform extracts a compound that is free from magnesium. The substance is easily purified by recrystallization from absolute alcohol. Analysis gave the following results :

I. 0.2002 gram substance gave 0.6126 gram CO_2 and 0.1135 gram H_2O .

II. 0.1497 gram substance gave 0.4590 gram CO_2 and 0.0868 gram H_2O .

	Calculated for $\text{C}_{22}\text{H}_{20}\text{O}_2$.	I.	Found.	II.
C	83.54	83.49		83.62
H	6.33	6.29		6.43

The molecular weight was determined in boiling acetone :

$$K = 1710.$$

Solvent. Grams.	Substance. Grams.	Elevation of boiling-point.	Molecular weight.
57.200	0.8010	0.083	322
	1.6400	0.167	328
	2.2990	0.237	324

Calculated for $C_{22}H_{20}O_2$.	Found.
316	324

The substance is methyl triphenylpropionate. It crystallizes in hard, lustrous plates that melt at 159° . It is readily soluble in chloroform and in boiling acetone, moderately so in boiling alcohol and in ether, insoluble in ligroin.

The phenyl group in the α -position evidently interferes with the ordinary reaction between esters and organic magnesium compounds as it was impossible to get either a ketone or a tertiary alcohol by boiling an ethereal solution of methyl triphenylpropionate with phenylmagnesium bromide. This probably accounts for the fact that no ketone is obtained when the unsaturated ester reacts with phenylmagnesium bromide.

Triphenylpropionic acid, $(C_6H_5)_2CHCHCO_2H$, was obtained

$$\begin{array}{c} | \\ C_6H_5 \end{array}$$

from the ester by hydrolysis. The ester is not easily hydrolyzed and it was necessary to boil it with alcoholic potassium hydroxide for six hours. The resulting acid was purified by recrystallization from aqueous alcohol. The analysis gave the following results:

0.1773 gram acid gave 0.5367 gram CO_2 and 0.0957 gram H_2O .

	Calculated for $C_{21}H_{18}O_2$.	Found.
C	82.78	82.55
H	6.00	5.99

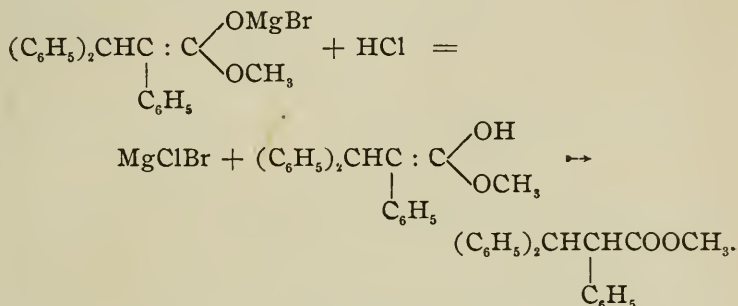
The acid crystallizes in needles that melt, without decomposition, at 211° . It is readily soluble in alcohol and in ether, sparingly so in ligroin, insoluble in water.

Ethyl triphenylpropionate was made by boiling the acid for eight hours with a 3 per cent solution of hydrochloric acid in absolute alcohol. It crystallizes in plates melting at 120° . An analysis gave the following results:

0.2320 gram ester gave 0.7155 gram CO_2 and 0.1393 gram H_2O .

	Calculated for $C_{23}H_{22}O_2$.	Found.
C	83.64	84.11
H	6.66	6.62

The magnesium compound, obtained by adding phenylmagnesium bromide to methyl phenylcinnamate, rapidly absorbs dry, gaseous hydrogen chloride. The products are methyl triphenylpropionate and magnesium chloride:



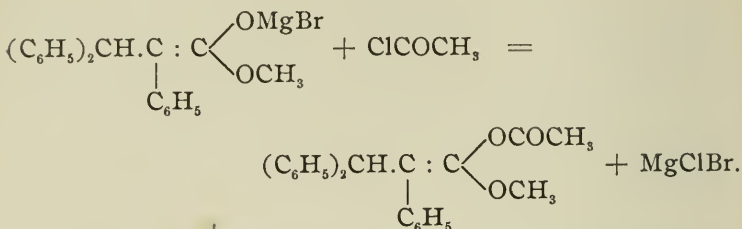
The magnesium compound readily reacts with acid chlorides but not with methyl iodide. A solution of 4 grams of acetyl chloride, in absolute ether, was added, gradually, to 10 grams of the magnesium compound, suspended in the same liquid. The substances combined at the ordinary temperature. As soon as all the acid chloride had been added, the ethereal layer was removed and washed with water until free from acetyl chloride. On evaporating the ether the product separated as a solid. This was purified by recrystallization from absolute alcohol. It is deposited in plates that melt at 75° . An analysis gave the following results:

0.1596 gram substance gave 0.5907 gram CO_2 and 0.1048 gram H_2O .

	Calculated for $C_{24}H_{22}O_3$.	Found.
C	80.44	81.12
H	6.14	5.91

The analytical results show that the substance has an acetyl group in place of a magnesium bromide residue. It is easily hydrolyzed; when boiled either with dilute acids or dilute

bases, acetic acid goes into solution and the solid methyl triphenylpropionate remains behind. The substance is, therefore, an acetate formed according to the equation :



Triphenylbromopropionic Ester, $(\text{C}_6\text{H}_5)_2\text{CHCHBrCOOCH}_3$. —
 $\begin{array}{c} | \\ \text{C}_6\text{H}_5 \end{array}$

The magnesium compound, described above, also readily reacts with bromine. Pure, dry bromine was added, from a dropping-funnel, directly to the mixture that had been obtained by bringing together equivalent quantities of methyl phenylcinnamate and phenylmagnesium bromide. The color of the bromine disappeared instantly, until the solution contained 1 molecule of bromine for every atom of magnesium used in the preparation of the phenylmagnesium bromide. The mixture was then poured into ice-water. Most of the product separated at once as a crystalline solid. The remainder was obtained by filtering, separating the ethereal layer and evaporating the ether. The solid was purified by solution in chloroform and precipitation with absolute alcohol. An analysis gave the following results :

0.1602 gram substance gave 0.3940 gram CO_2 and 0.0601 gram H_2O .

	Calculated for $\text{C}_{22}\text{H}_{19}\text{O}_2\text{Br}$.	Found.
C	66.86	67.07
H	4.05	4.10

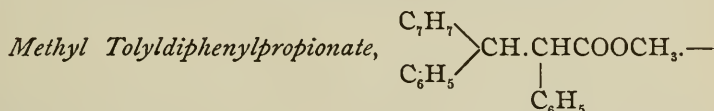
The ester is readily soluble in chloroform and in boiling acetone, slightly in alcohol and in ether. It crystallizes in large, colorless prisms and melts, with decomposition, at 150° – 152° .

Triphenylacrylic Acid, $(\text{C}_6\text{H}_5)_2\text{C} : \text{CCO}_2\text{H}$.—When methyl



triphenylbromopropionate is boiled with alcoholic potassium hydroxide it is slowly transformed into the potassium salt of triphenylacrylic acid. In order to get a product that was free from bromine and completely soluble in water it was necessary to boil for three hours. The reaction is a very clean one. The crude acid, precipitated by acidifying the aqueous solution remaining after distilling off the alcohol, was colorless and melted at 210° to 211° . After one crystallization from alcohol it melted at 213° —the melting-point of pure triphenylacrylic acid. The acid is identical with that obtained by V. Meyer and Stahl by condensing benzophenone chloride with phenylacetic acid, as it gives brilliant red crystals of diphenylindone when heated at 200° with zinc chloride.

Reaction with Orthotolylmagnesium Bromide.



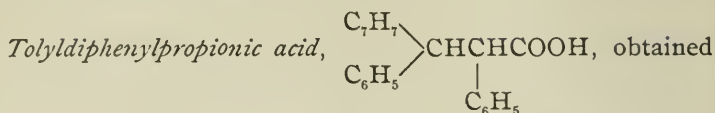
Equivalent quantities of the reagents were brought together as described under the reaction with phenylmagnesium bromide. The addition-product separated from the liquid in colorless crystals. The ester, obtained by decomposing the magnesium compound with water, was purified by crystallization from a mixture of alcohol and acetone. It is deposited in hard, lustrous plates melting at 150° . An analysis gave the following results :

0.1743 gram substance gave 0.5337 gram CO_2 and 0.1054 gram H_2O .

	Calculated for $\text{C}_{23}\text{H}_{22}\text{O}_2$.	Found.
C	83.63	83.57
H	6.66	6.71

As the ester contains two dissimilar, asymmetric carbon atoms it is capable of existing in two inactive stereoisomeric modifica-

tions. We examined the mother-liquors carefully but failed to find a second product of the reaction.

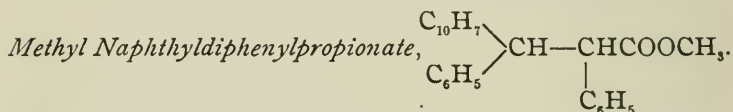


by saponifying the ester with alcoholic potash, was purified by recrystallization from aqueous alcohol. It melts at 190° and is deposited in long needles. The analysis gave the following results :

0.1681 gram substance gave 0.5140 gram CO_2 and 0.1014 gram H_2O .

	Calculated for $\text{C}_{22}\text{H}_{20}\text{O}_2$.	Found.
C	83.54	83.39
H	6.33	6.70

Reaction with α -Naphthylmagnesium Bromide.



—The substances were brought together in boiling ethereal solution. The addition-product separated as a colorless oil that solidified on cooling. When this solid was decomposed with dilute hydrochloric acid it gave a mixture of esters that was extremely difficult to separate. The best results were obtained as follows : The liquid, in which the addition-product from 25 grams of methyl phenylcinnamate was suspended as an oil, was diluted to a liter with ordinary ether and immediately poured into iced hydrochloric acid. The ethereal layer was removed and shaken with cold water until a solid began to deposit as a hard crust on the walls of the separating-funnel. The liquids were then allowed to stand without further shaking until the amount of solid no longer increased—from eighteen to twenty-four hours. The solid consisted mainly of the higher melting ester which was obtained pure by several recrystallizations from a mixture of ethyl acetate and alcohol. The analyses show that it is a methyl naphthylldiphenylpropionate.

I. 0.1070 gram substance gave 0.3322 gram CO_2 and 0.0592 gram H_2O .

II. 0.1667 gram substance gave 0.5220 gram CO_2 and 0.0905 gram H_2O .

	Calculated for $\text{C}_{26}\text{H}_{22}\text{O}_2$.	Found.	
		I.	II.
C	85.26	84.95	85.07
H	6.00	6.15	6.03

The ester melts at 170° , is readily soluble in chloroform, acetone and ethyl acetate, slightly so in alcohol, ether and boiling ligroin. It crystallizes in small, lustrous pyramids or prisms.

The ethereal solution, from which this ester had separated, contained some more of the same substance, mixed with a lower melting ester, some dinaphthyl and a small quantity of naphthalene. The last two were removed by evaporating the ether and repeatedly extracting the residue with cold alcohol. A partial separation of the esters was effected by careful recrystallization from a mixture of ethyl acetate and alcohol. The lower melting derivative was finally obtained in perfectly pure condition by recrystallization from boiling absolute alcohol. The following analyses show that it is isomeric with the higher melting ester :

I. 0.1115 gram substance gave 0.3480 gram CO_2 and 0.0605 gram H_2O .

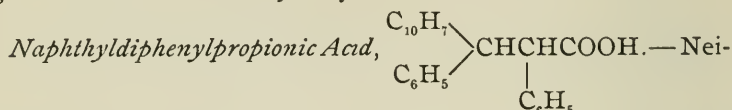
II. 0.1227 gram substance gave 0.3825 gram CO_2 and 0.0666 gram H_2O .

	Calculated for $\text{C}_{26}\text{H}_{22}\text{O}_2$.	Found.	
		I.	II.
C	85.20	85.29	85.01
H	6.00	6.03	6.05

This compound melts at 128° and is considerably more soluble in organic solvents than its isomer (m. p. 170°), dissolving readily in acetone, chloroform, ethyl acetate and boiling alcohol, moderately in cold alcohol and in ether. It crystallizes in large lustrous prisms.

Naphthyldiphenylpropionic acid, like orthotolyldiphenylpropionic acid, has two unequal, asymmetric, carbon atoms, and

is, consequently, capable of existing in two inactive modifications. The two esters described above may, therefore, be stereoisomers, but, if they are, the component acids are mutually transformed more easily than is usually the case with substances that bear this relation ; although neither ester could be converted into its isomer by heating, the two invariably gave the same acid on hydrolysis.



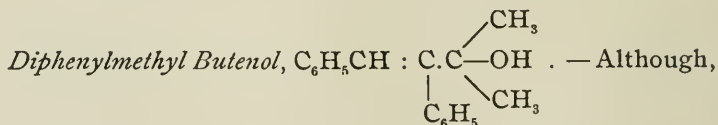
ther of the esters yields the acid easily. Each of them was hydrolyzed by allowing a solution in concentrated alcoholic potassium hydroxide to stand for some weeks at the ordinary temperature, by boiling for six hours with alcoholic potassium hydroxide, or by heating at 150° , with concentrated hydrochloric acid, in sealed tubes. The same acid was obtained in every experiment—a substance crystallizing in short, thick needles, melting at 171° . The acid was purified from aqueous alcohol. Analysis gave the following results :

0.1388 gram substance gave 0.4331 gram CO_2 and 0.0712 gram H_2O .

	Calculated for $\text{C}_{25}\text{H}_{20}\text{O}_2$.	Found.
C	85.23	85.01
H	5.68	5.70

This acid, apparently, corresponds to the lower melting ester, as only this one is obtained when the acid is boiled, during eight hours, with 3 per cent solution of hydrochloric acid in methyl alcohol.

Reaction with Methylmagnesium Iodide.



as shown above, the phenyl group in the α -position undoubtedly interferes with the reaction between an ester and phenylmagnesium bromide, it seems to have no effect on that between an ester

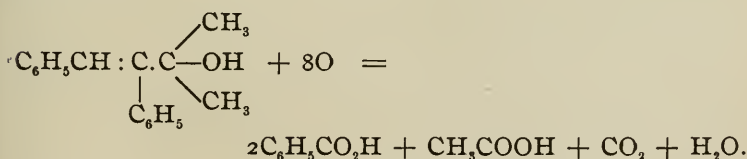
and methylmagnesium iodide. The sole product of the reaction between this substance and methyl α -phenylcinnamate is, the magnesium derivative of a tertiary alcohol. The experiment was tried at various temperatures, between the one given by an efficient freezing-mixture and that of boiling benzene, without any difference in the result. The product, isolated in the usual way, is a solid, melting at 68° . It was purified by recrystallization from a mixture of ether and ligroin. The analyses gave the following results :

I. 0.1772 gram substance gave 0.5562 gram CO_2 and 0.1227 gram H_2O .

II. 0.1608 gram substance gave 0.5050 gram CO_2 and 0.1101 gram H_2O .

	Calculated for $\text{C}_{17}\text{H}_{18}\text{O}$.	I.	Found.
C	85.71	85.60	85.65
H	7.56	7.75	7.60

The substance liquefies when brought in contact with a small quantity of alcohol. It is readily soluble in acetone and ether, moderately so in low-boiling ligroin. It crystallizes from ether in thin plates, from ligroin in long flat needles. The presence of the hydroxyl group was established by the method of Tzugaieff; the substance instantly decomposes a solution of methylmagnesium iodide, with evolution of an inflammable gas. The presence of the double union is shown by the ease with which the compound is oxidized by alkaline permanganate. The oxidation was carried out at the ordinary temperature, but the only products obtained were benzoic acid and acetic acid :



The alcohol does not combine with bromine and no bromine derivative is obtained when the magnesium compound, cor-

responding to the alcohol, is treated with bromine before it is decomposed with water.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
October, 1904.

FORMATION OF ACIDS BY ENZYMES.

BY J. E. HINKINS.

It has been shown that nuclein, leucine, xanthine and many volatile fatty acids, together with acid phosphates and bicarbonates, are present in small quantity in normal saliva. The quantities vary very greatly with the individual and probably also depend on the age and state of health, because, in abnormal constitutional conditions, the usual proportions may be greatly increased.

The rôle of the ptyaline in the generation of these organic acids must be very important, as the saliva contains a large number of substances that give rise to acids when hydrolyzed by the enzymes. Constitutional changes tending to cause the enzymes to become especially abundant naturally, result in the saliva becoming more markedly acid, unless there are counteracting influences.

The following experiments show how relatively large is the production of acids by enzymes :

Glucose (40 grams) and acetic anhydride (120 grams) were heated on a water-bath half an hour, to dissolve the glucose. The solution was then poured into 250 cc. of hot water, evaporated to about one-third of its original volume, neutralized with N/KOH solution and diluted to 1 liter. Two hundred and fifty cc. of this solution, together with 50 cc. of 1 per cent bouillon, were treated with 5 grams of ptyaline or pancreatin. The liquids were placed in an ice-box, a check was kept on the original triacetyl glucose solution and all of them were maintained sterile by means of toluene and thymol.

Ptyaline Solution.

Time in days.	N/10 KOH required for 10 cc. solution. cc.	N/10 KOH required for original triacetyl glucose solution. cc.
0	. .	2.50
5	7.50	3.00
9	8.50	3.50
17	11.00	4.00
26	13.00	4.60
32	13.90	4.75

Enzyme Filtered Out.

40	13.75	5.50
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Pancreatin Solution.

Time in days.	N/10 KOH required for 10 cc. solution. cc.	N/10 KOH required for original triacetyl glucose solution. cc.
0	. .	2.50
5	8.00	3.00
9	9.00	3.50
17	12.00	4.00
26	14.50	4.60
32	14.84	4.75

Enzyme Filtered Out.

40	14.75	5.50
----	-------	------

In order to learn the combined effect of bacteria and enzymes on the peptone solution, both of the above liquids, containing pancreatin and ptyaline, were treated with cultures of bacteria taken from the mouths of individuals having severe cases of tooth erosion. The solutions were kept at 37°, the body temperature, and titrated at intervals. It will be seen from the following tables that, even in a shorter time, the presence of the bacteria causes a rise in acidity :

Ptyaline Solution.

Time in days.	N/10 KOH for 10 cc. solution, cc.
6	9.50
14	12.00
21	13.75

Pancreatin Solution.

Time in days.	N/10 KOH for 10 cc. solution. cc.
6	11.25
14	16.50
21	19.00

After filtration from the enzyme the solutions mentioned on page 165 resembled bacteria-free saliva in composition, differing only in being a little more acid. Portions of these solutions were treated with pellets of Harvard cement, which had been made as usual for teeth-fillings and had set, and also with the finely powdered material, obtained by grinding up other pellets. The solutions were allowed to stand several days, at 0°, and the loss in weight of the cement was then determined. The following data were obtained :

Ptyaline Solution.

Time. Days.	Volume of ptyaline solution. cc.	Weight of cement. Gram.	Loss. Gram.
0	50	0.6793 (pellet)	. .
8	50	0.6505 "	0.0288
0	50	1.000 (powdered)	. .
8	50	0.927 "	0.0730

Pancreatin Solution.

Time. Days.	Pancreatin solution. cc.	Weight of cement. Gram.	Loss. Gram.
0	50	0.5767 (pellet)	. .
8	50	0.5400 "	0.0367
0	50	1.000 (powdered)	. .
8	50	0.860 "	0.140

From the above tables it is very evident that the solutions made acid by enzymes can readily dissolve the Harvard cement, the more rapidly the greater the acidity of the solution.

The following results show that the acidity of the saliva of individuals with marked erosion of the teeth is much greater than that of those not so affected. The mouth was thoroughly cleaned with a tooth-brush and dilute alcohol ; the saliva was then collected as rapidly as possible, kept cold with ice and titrated at once when 10 cc. had been obtained.

		K/10 KOH for 10 cc. saliva. cc.
Case 1.	No erosion	0.34
" 2.	Slight erosion	0.70
" 3.	Decided erosion for twelve years	1.32
" 4.	" " " two years	1.40
" 5.	Very decided erosion for three years, extending from molar to molar	1.94

Conclusions.

1. Solutions of triacetylglucose are made acid by the action of certain enzymes.
2. The acidity is increased by the simultaneous presence of bacteria.
3. Such acid solutions readily dissolve cements employed for tooth fillings.
4. The abnormal increase in the acidity of the saliva of persons suffering from tooth erosion is probably due to the resolution of certain constituents of the saliva by enzymes.

CHICAGO, September 1, 1904.

Contributions from the Chemical Laboratory of Harvard College.

ON THE DISSOCIATION OF PHENOQUINONE AND QUINHYDRONE.¹

BY HENRY A. TORREY AND H. HARDENBERGH.

The fact that phenoquinone, which in the solid state is red and quinhydrone, which is green, both dissolve in organic solvents, with the formation of a yellow solution, is highly suggestive of the idea that, in dissolving, they have become dissociated into quinone and phenol and quinone and hydroquinone, respectively.

Molecular weight determinations in benzol have shown this to be the case. For a long time it has been recognized that these two substances are very unstable; that they are easily decomposed by acids or alkalies. Hesse² says that quinhydrone

¹ A number of years ago some preliminary work on the dissociation of phenoquinone and quinhydrone was done by one of us and Mr. G. S. Brand at the University of Vermont.

² Ann. Chem. (Liebig), 200, 243.

is somewhat decomposed by boiling chloroform and Clark¹ observes that all solvents dissociate it to some extent. Biltris,² in connection with the study of the preparation of some compounds of this nature, found, by molecular weight determinations, that *p*-cresophenoquinone, a mixed phenoquinone, is dissociated in benzol and that ordinary phenoquinone and quinhydrone undergo the same change in ether. These articles did not come to our attention until after our own work was completed, but the results which we give, although confirmatory of Biltris's work, do not cover the same ground. Much of our time was spent in attempting to show a reassociation of the products of dissociation, by the addition of one of the dissociation-products, thus proving the nature of this dissociation.

Preparation of the Material.

The quinone used in the investigation was purified by crystallization from ligroin and the hydroquinone by crystallization from water. The phenol was distilled fractionally and that fraction coming over at 180°–181° was used. The phenoquinone was made by adding two molecules of phenol, dissolved in purified ligroin, to one molecule of quinone in the same solvent. The phenoquinone separated out in beautiful red crystals, which were carefully washed with ligroin. It was not found advantageous to attempt to recrystallize the product. In this connection it may be interesting to note that phenoquinone is formed at the ordinary temperature, when the *vapors* of phenol and quinone are allowed to come in contact. If, for example, two test-tubes, containing, respectively, phenol and quinone, are connected by a bulb-tube, red crystals of phenoquinone will appear in the bulb and connecting-tube.

In the preparation of quinhydrone it was found advantageous to mix ethereal solutions of quinone and hydroquinone, in molecular proportions, rather than to oxidize hydroquinone with ferric chloride, as the product obtained by the latter method was likely to contain iron.

The benzol was purified by shaking thoroughly with concen-

¹ THIS JOURNAL, 14, 574.

² Acad. Roy. d. Belgique [3], 32, 300; 35, 60.

trated sulphuric acid. It was then allowed to stand, first over sodium carbonate, then over calcium chloride and finally was completely dried with metallic sodium.

Dissociation of Phenoquinone and Quinhydrone.

The determination of the molecular weights of phenoquinone and quinhydrone, in benzol, were carried out by the regular boiling- and freezing-point methods. Phenoquinone was first and most thoroughly studied, but before undertaking the investigation of the condition of this substance, the molecular weights, in benzol, of phenol and quinone, its two dissociation-products, were determined. The molecular weights are calculated from the well-known formula, $M = \frac{100 Ks}{Wx}$.

In the tables given below the concentration is given in grams of dissolved substance in 100 grams of the solvent. The first determinations were made by the boiling-point method.

Molecular Weight of Phenol in Benzol by the Ebullioscopic Method.

I.				
W.	s.	x.	K.	M.
100	1.1635	0.306	26.7	102
. .	2.4023	0.620	. .	104
. .	4.0857	1.009	. .	108
. .	5.5599	1.320	. .	112

II.				
100	1.5788	0.402	26.7	105
. .	3.6347	0.885	. .	120
. .	6.8754	1.516	. .	118
. .	10.1402	2.215	. .	122

III.				
100	1.7681	0.459	26.7	103
. .	4.1897	1.016	. .	110
. .	8.0288	1.826	. .	117
. .	13.0903	2.801	. .	125

As the molecular weight of phenol is 94, it is evident that phenol is somewhat polymerized at the boiling-point of benzol. The results of Beckmann,¹ Auwers² and others, obtained by

¹ Z. physik. Chem., 2, 715.

² *Ibid.*, 12, 696.

cryoscopic methods, show that the phenol is polymerized even at low concentrations and that this polymerization increases with the concentration. We made some determinations by this method because it was desirable to know the molecular weight of phenol at as many concentrations as possible for the study of the action of the dissociation-products on phenoquinone.

Molecular Weight of Phenol by the Cryoscopic Method.

I.

W.	s.	x.	K.	M.
100	1.1715	0.344	49	167
. .	2.0831	0.610	.	168
. .	3.0401	0.862	.	173
. .	4.6250	1.234	.	183

II.

100	1.9441	0.595	49	160
. .	4.7603	1.361	.	171
. .	8.6830	2.248	.	189
. .	11.8323	2.855	.	203

III.

100	1.1874	0.376	49	155
. .	6.0981	1.686	.	177
. .	8.2911	2.181	.	186
. .	13.1507	3.109	.	207

Molecular Weight of Quinone by the Ebullioscopic Method.

I.

W.	s.	x.	K.	M.
100	0.6419	0.161	26.7	106
. .	1.5302	0.360	. .	114
. .	2.1083	0.466	. .	121
. .	2.6102	0.577	. .	121

II.

100	1.0029	0.245	26.7	109
. .	3.1760	0.732	. .	117
. .	6.7831	1.538	. .	118
. .	9.5189	2.080	. .	122

III.

W.	s.	x.	K.	M.
100	2.7023	0.640	26.7	112
. .	4.1352	0.955	. .	116
. .	6.8541	1.561	. .	117
. .	9.1456	2.077	. .	118

The average of all these determinations is 116.

Molecular Weight of Quinone by the Cryoscopic Method.

W.	s.	x.	K.	M.
100	1.3652	0.648	49	104
. .	3.7575	1.734	.	106
. .	5.7099	2.608	.	104

Average, 105

The cryoscopic determinations agree with those of Auwers,¹ which show that the molecular weight of quinone is not affected by the concentration.

The determinations of the molecular weight of phenoquinone, as given below, show that it is highly dissociated in benzol, as Biltris had already found it to be in ether.

Molecular Weight of Phenoquinone by the Ebullioscopic Method.

W.	s.	x.	K.	M.
100	1.2365	0.317	26.7	109
. .	2.7037	0.657	. .	110
. .	4.3726	1.033	. .	113
. .	6.5794	1.468	. .	120

Molecular Weight of Phenoquinone by the Cryoscopic Method.

I.

W.	s.	x.	K.	M.
100	0.3407	0.137	49	121
. .	0.9674	0.367	.	129
. .	1.9577	0.700	.	137
. .	3.3345	1.126	.	145

II.

100	1.1310	0.393	49	141
. .	2.8953	0.959	.	148
. .	3.8622	1.211	.	153

Although the above molecular weights found for phenoquinone

¹ *Loc. cit.*

are larger than its molecular weight, 296, by one-third, this does not show incomplete dissociation, as the phenol, which would be formed on dissociation, is somewhat polymerized in the solvent used. The actual degree of dissociation could be arrived at by employing the following formula :

$$\gamma = \frac{t - t_0}{t_1 - t_0},$$

in which γ is the degree of dissociation, t the actual elevation, t_0 the theoretical elevation or depression, provided there were no dissociation, and t_1 the elevation or depression that would be caused by complete dissociation. In obtaining t_1 the actual amounts of phenol and quinone in a given weight of phenoquinone are calculated and the molecular weights corresponding to these concentrations are used instead of the values 94 and 108 and from these actual molecular weights, t_1 is calculated on the basis of complete dissociation.

The table below gives the elevation of the boiling-point, or the depression of the freezing-point, due to phenol alone and to quinone alone, provided the phenoquinone were completely dissociated, the sum of these two values, which is t_1 , and, in the last column, the actual change produced by phenoquinone itself, which is t .

The molecular weights of phenol for the different concentrations are taken from the results already given, or from the work of Auwers or Beckmann, either directly, by interpolation, or by taking averages. It will be seen that the actual rise, t , is nearly equal to that calculated for complete dissociation, t_1 .

By the cryoscopic method Auwers found 143 to 164 as the molecular weight of phenol, in concentrations ranging from 0.51 to 3.93 per hundred and Beckmann 144 to 252 in concentrations 0.337 to 26.77 per hundred.

Although, from the nature of the case, it can hardly be doubted that the dissociation-products are quinone and phenol, this was shown to be the fact by the ease with which phenoquinone is "salted out" from solution by the addition of either of these substances in excess of the solubility-product.

*Phenoquinone and Quinhydrone.**Table I.—Ebullioscopic Method.*

Weight of phenoqui- none in 100 grams of benzol.	Molecular weight found.	Weight of phenol in grams.	Weight of quinone.	Molecular weight of phenol.	Molecular weight of quinone.	Rise due to phenol.	Rise due to quinone.	Sum, t_1 .	Actual rise, t_2 .
1.237	109	0.785	0.451	100	115	0.209	0.105	0.314	0.317
1.711	112	1.087	0.624	103	..	0.283	0.145	0.428	0.409
2.704	110	1.717	0.987	104	..	0.441	0.229	0.670	0.657
4.373	113	2.777	1.596	107	..	0.693	0.370	1.063	1.033
6.579	120	4.179	2.401	110	..	1.012	0.557	1.569	1.468
<i>Cryoscopic Method.</i>									
0.9674	129	0.6144	0.3530	140	104	0.215	0.167	0.382	0.367
1.1310	141	0.7183	0.4127	142	..	0.248	0.195	0.443	0.393
1.9577	137	1.2433	0.7144	148	..	0.412	0.337	0.749	0.700
2.8453	148	1.8388	1.0565	157	..	0.574	0.497	1.071	0.959
3.3345	145	2.1178	1.2167	159	..	0.652	0.573	1.225	1.126
3.8622	153	2.4528	1.4094	161	..	0.747	0.661	1.411	1.241

The solvent chosen was ligroin, on account of the rather low solubility of phenoquinone in that liquid. A saturated solution was prepared and a weighed quantity of phenol added. The separation of the phenoquinone was considerable, but not proportional to the phenol added; no attempt was made to get very accurate quantitative results. Volume of solution used, 25 cc.; weight of phenol added, 0.0500 gram; weight of phenoquinone precipitated, 0.0340 gram. Of course the phenol is by no means all present in the monomolecular condition.

The action of the dissociation-products on dissolved phenoquinone was next studied by cryoscopic and ebullioscopic methods. If the dissociation is hindered by the addition of either phenol or quinone, it should be indicated by the freezing- or boiling-point of the solution, provided this hindrance is not too slight, for the elevation or depression produced by the addition of phenol, say, to a solution of phenoquinone, should be somewhat less than that calculated for the weight of phenol added.

That reassociation of the quinone and phenol apparently does take place when phenol is added is shown in the table given below. In the first horizontal column are given the data from phenoquinone itself. The vertical columns, VI. and VII., show the rise which should be due to phenol and quinone, respectively, on the facts of complete dissociation; in column VIII. the sum of these two values; and in column IX. the actual rise. The rise due to phenol is calculated from the molecular weight as actually found, either directly or by interpolation, for the concentration in question and not from the molecular weight 94. The molecular weight 115, the average of a number of determinations already given above, is used for quinone.

It will be observed that the actual rise is always less, and increasingly so, than the sum. The difference is, however, not very great. The solution became redder as the phenol was added.

The freezing-point method (Table III.) gave similar results.

Table II.—*Ebullioscopic Method.*

	I. Weight of substance in 100 grams benzol.	II. Weight of phenol.	III. Weight of quinone.	IV. Molecular weight of phenol.	V. Molecular weight of quinone.	VI. Rise due to phenol.	VII. Rise due to quinone.	VIII. Sum of VI. and VII.	IX. Actual rise.
Phenoquinone	1.7110	1.0868	0.6242	104	115	0.279	0.145	0.424	0.409
Phenoquinone and phenol	3.5103	2.8861	0.6242	107	115	0.720	0.145	0.865	0.821
	4.8578	4.2336	.	112	.	1.010	0.145	1.155	1.121
	8.4705	7.8463	.	117	.	1.790	0.145	1.935	1.857

Table III.—Cryoscopic Method.

I.								
	I. Weight of substance in 100 grams of benzol.	II. Weight of phenol.	III. Weight of quinone.	IV. Molecular weight of phenol.	V. Molecular weight of quinone.	VI. Depression due to phenol.	VII. Depression due to quinone.	VIII. Sum of VI. and VII.
Phenoquinone	0.6194	0.3933	0.2261	140	104	0.138	0.107	0.245
Phenoquinone and phenol	2.7241 6.1396 9.7526	2.4980 5.9135 9.5265	0.2261 . .	161 173 193	104 . .	0.761 1.675 2.419	0.107 . .	0.868 1.782 2.526
Phenoquinone	2.1960	1.3945	0.8015	153	104	0.447	0.378	0.825
Phenoquinone and phenol	5.3600 7.6380 13.9600	4.5585 6.8365 13.1585	0.8015 . .	170 181 207	104 . .	1.314 1.851 3.115	. . .	1.692 2.229 3.493
								IX. Actual depression.
								0.234 0.829 1.688 2.469 0.762 1.550 2.041 3.200

II.

Table IV.—Effect of the Addition of Quinone—Cryoscopic Method.

	I. Weight of substance in 100 grams of benzol.	II. Weight of phenol.	III. Weight of quinone.	IV. Molecular weight of phenol.	V. Molecular weight of quinone.	VI. Depression due to phenol.	VII. Depression due to quinone.	VIII. Sum of VI. and VII.	IX. Actual depression.
Phenoquinone	2.6470	1.6808	0.9662	156	104	0.528	0.455	0.983	0.920
Phenoquinone and quinone	4.6277	1.6808	2.9469	156	104	0.528	1.396	1.924	1.773
	7.1560	. .	5.4752	. .	. .	0.528	2.580	3.108	2.721
	9.8558	. .	8.1750	. .	. .	0.528	3.852	4.380	3.510

Similar results were also obtained when quinone, the other dissociation-product (Table IV.), was added.

In the above table the molecular weight of quinone is taken as 104, although determinations were not made at such high concentrations; further, it will be noticed that, on the last addition of quinone, the difference between the actual depression and that calculated on the basis of complete dissociation is greater than could be accounted for by complete reassociation of the phenoquinone. It may be that the quinone, the phenoquinone, or both, are somewhat polymerized.

Dissociation of Quinhydrone.

Quinhydrone being much less soluble in most media than phenoquinone, it was not easy to find a suitable solvent. Although ethyl acetate dissolves quinhydrone, great difficulty was found in the determination of the dissociation by the boiling-point method and as the time was short, a single determination was made in benzol, which, although the concentration was very small, shows that quinhydrone is highly dissociated.

W.	s.	x.	K.	M.
100	0.3363	0.090	26.7	100
. .	0.5180	0.115	. .	120
. .	0.6078	0.130	. .	125

As the theoretical molecular weight of quinhydrone is 218 and those of quinone and hydroquinone 108 and 110, respectively, it is evident that quinhydrone is practically completely dissociated in benzol, as was shown by Biltris for ether.

Action of Chloroform on Quinhydrone.

When quinhydrone is dissolved in warm chloroform and then allowed to cool slowly, a white substance separates rather abundantly at about 35°. This was collected on a Gooch crucible, washed with a little more chloroform and was shown by its melting-point (169°) to be pure hydroquinone. If the temperature is allowed to fall below 35° quinhydrone itself begins to appear. Like phenoquinone, quinhydrone may be precipitated from its solutions by addition of one of its dissociation-products.

Although determinations of the molecular weight of phenoquinone and quinhydrone were made in benzol only, the color of solutions of these substances in a large number of solvents was observed and showed the general dissociation of these compounds.

Color of Phenoquinone and Quinhydrone in Various Solvents.

Solvent.	Phenoquinone.	Quinhydrone.
Acetone	Yellow	Yellow
Ethyl alcohol	"	"
Methyl "	"	"
Amyl "	"	"
Ether	"	"
Toluol	"	"
Benzol	"	"
Chloroform	"	"
Carbon disulphide	"	"
Ligroin	"	Insol.
Ethyl acetate	"	Yellow
Methyl "	"	"
Water	"	"

In the case of the alcohols the phenol was dissolved first from the phenoquinone even in the cold, leaving the yellow quinone behind, which could then be brought into solution by shaking.

As phenoquinone and quinhydrone are dissociated in organic solvents it is evident that the reactions of these bodies in solution could hardly be relied on for the determination of their constitution: one is dealing, in the one case, with a mixture of quinone and phenol and in the other of quinone and hydroquinone; moreover, any formulas properly representing the constitution of these bodies must be in accordance with their easy dissociation.

Studies are being made in this laboratory of the condition in solution of the compounds discovered by Edeleanu and Eulescu,¹ which are formed from *p*-nitrosodimethylaniline and certain monatomic and diatomic phenols, and are apparently analogous to phenoquinone and quinhydrone.

¹ J. Chem. Soc., 70, i, 359 (1896).

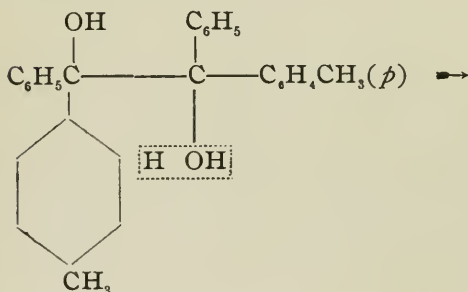
Preliminary Contribution from Johns Hopkins University.
ON THE PINACONE-PINACOLIN REARRANGEMENT.¹

BY S. F. ACREE.

The articles by Werner and Grob² and by Dilthey and Last³ make it necessary to write this notice; a more detailed account of the work will appear later.

As indicated in two articles recently published,⁴ I have undertaken an exhaustive study of the pinacone-pinacolin rearrangement and am investigating this interesting problem from several points of view. In trying to ascertain the cause and mechanism of the reaction, various classes of pinacones, pinacolins and similar substances are being made by the methods already outlined and are being studied carefully.

One of the first things that I shall try to ascertain is whether the pinacone, pinacolin, or other similar rearrangements, can take place through ring formation, as first suggested by Couturier⁵ and subsequently by Klinger and Lounes⁶ and by Zelinsky and Zelikow.⁷



¹ This work was made possible by a grant from the Carnegie Institute of Washington.

² Ber. d. chem. Ges., **37**, 2887.

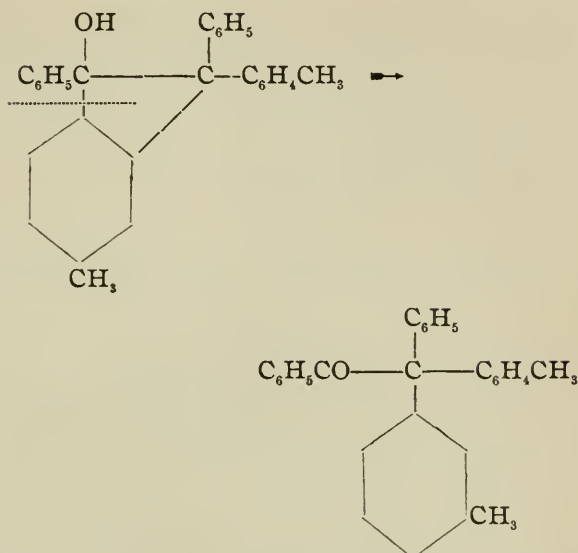
³ *Ibid.*, **37**, 2639.

⁴ *Ibid.*, **37**, 2753, 2764.

⁵ Ann. chim. phys., [6], **26**, 433.

⁶ Ber. d. chem. Ges., **29**, 2160.

⁷ *Ibid.*, **34**, 3249.



If this be the course of the reaction, a *p*-tolyl group that changes its position from one of the glycol carbon atoms to the other must become a *m*- or *o*-tolyl group. Likewise, a migrating *o*- or *m*-tolyl radicle might become a *p*-, *m*- or *o*-tolyl complex and a tertiary butyl would become an isobutyl group. A large number of pinacones, symmetrical and unsymmetrical, will be rearranged and studied to learn if, in any case, a change in the character of the migrating group takes place.

As directly connected with this problem, I am also investigating the rearrangement of α, α -dialkyl dihalogen ethanes,¹

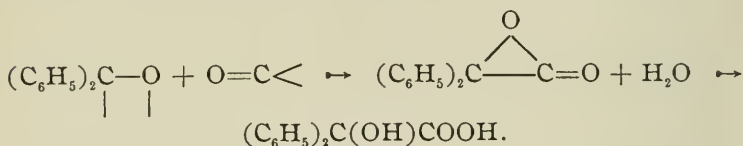


into tolane derivatives, $RC \equiv CR$ and of the corresponding trichlor compounds, $R_2CH.CX_3$, into dialkylethylene.² The rearrangement of geometrical isomers of the following type, $RR_1C = CHCl$ and similar substances, will be investigated with special care.

¹ Fritsch : Ann. Chem. (Liebig), **279**, 319.

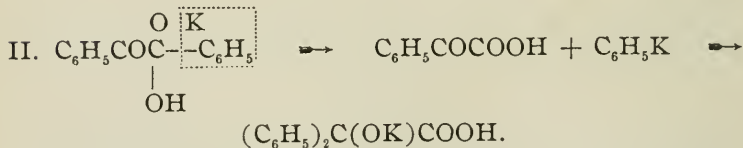
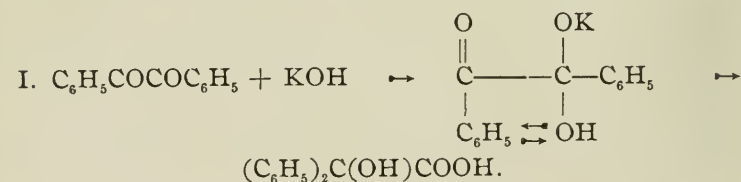
² Elbs and Förster : J. prakt. Chem., **39**, 298 ; **47**, 44. Goldschmidt : Ber. d. chem. Ges., **6**, 985 ; Hepp : *Ibid.*, **7**, 1409.

In this connection the rearrangement of benzil homologues into benzilic acid derivatives seems to be of great interest. Nef¹ has recently suggested that this depends upon the dissociation of benzil into nascent carbon monoxide and benzophenone; these then reunite to give an α -lactone, which takes up water, yielding benzilic acid.



When benzophenone is heated at 250° with formic acid, potassium formate, or formic ester, no benzilic acid is produced, although this should be the case if Nef's hypothesis were correct.

The following suggestion is, therefore, offered tentatively and will be subjected to experimental proof. The benzil may unite with the alkali² to form a pinacone-like addition-product, which then rearranges into benzilic acid, somewhat according to one of the two following schemes:



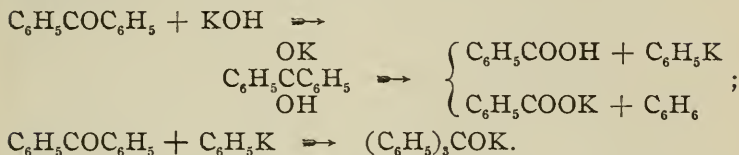
The recent work of Delange³ is in harmony with the second series of reactions. When benzophenone was heated at 170° with dried potassium hydroxide, benzene, benzoic acid and

¹ Ann. Chem. (Liebig), **335**, 272.

² Chancel: *Ibid.*, **72**, 279.

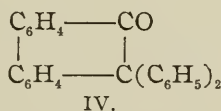
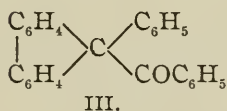
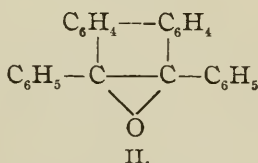
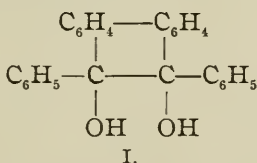
³ Bull. soc. chim., [3], **29**, 1131.

triphenyl carbinol were obtained. It is very probable that the action takes place as follows :



These reactions are in entire harmony with the views of Nef¹ and with my own work² on sodium phenyl and similar compounds.

In continuation of my work on the preparation of pinacones by the addition of sodium phenyl or phenylmagnesium bromide to 1,2-diketones,³ I have prepared dihydroxydiphenyldihydrophenanthrene, the corresponding di-*p*-tolyl compound and dihydroxydiphenyldihydroacenaphthene, by the action of phenylmagnesium bromide on phenanthrenequinone and acenaphthenequinone, respectively. These substances were rearranged into the corresponding pinacolins by heating with acetyl chloride. The dihydroxydiphenyldihydrophenanthrene (I.) could rearrange into the anhydride-like α -pinacolin (II.), or into two β -pinacolins—benzoylphenylfluorene (III.), or diphenylphenanthrone (IV.).



When the dihydroxydiphenyldihydrophenanthrene (I.) is heated during several hours with acetyl chloride it changes into a product that melts at 198° (Werner and Grob⁴ give 194°—

¹ Ann. Chem. (Liebig), 298, 310. *see errata p. 647*

² THIS JOURNAL, 29, 588; Ber. d. chem. Ges., 37, 2753.

³ Loc. cit.

⁴ Ber. d. chem. Ges., 37, 2903.

196°) and has the formula $C_{26}H_{18}O$. As this is not identical with benzoylphenylfluorene¹ (III.), m. p. 172°, it must have the formula II. or IV. In favor of formula IV. are the following facts: α -Pinacolins are very easily oxidized by chromic acid, in boiling glacial acetic acid, to the corresponding ketones. But the pinacolin, m. p. 198°, which I obtain is not appreciably affected by this oxidizing mixture during thirty minutes. Furthermore, when this pinacolin is heated with alcoholic potassium hydroxide it easily yields the salt of an acid which is most probably diphenylmethyl-*o,o*-phenyl benzoic acid,



The formation of this from the substance with formula IV. would be expected, but an α -pinacolin (II.) would probably not give such an acid, unless a further rearrangement were to occur. It seems, therefore, that both of these facts point decidedly to formula IV. for the compound. On the other hand, Werner and Grob² believe this substance to have the formula II., their chief evidence being that it gives 9,10-diphenylphenanthrene when distilled with zinc dust. It is well known that, when β -pinacolins are vigorously reduced, they tend to rearrange and give symmetrical derivatives and I doubt if Werner and Grob are warranted in assuming the formula II. for the compound.

I am now engaged in attempting the synthesis of this pinacolin and of the acid obtained from it, from *o*-diphenic acid and by other means that should give definite conclusions as to its constitution. I shall also treat various derivatives of phenanthrenequinone, acenaphthenequinone, crysenequinone, etc. with Grignard's reagent and investigate the rearrangement of the resulting pinacones (I.) and pinacolins (IV.), to see if the migrating groups change in character.

These syntheses have been further extended to the formation of tetralkylglycols,



by the action of Grignard's reagent on 1,3-, 1,4-, 1,5-dike-

¹ Klinger and Lounes: Ber. d. chem. Ges., 29, 2152.

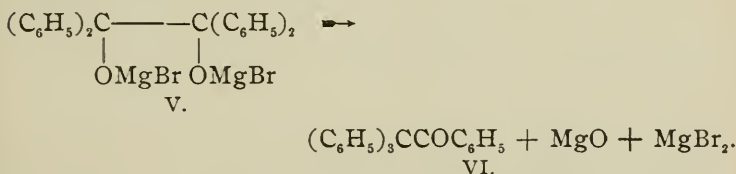
² *Ibid.*, 37, 2893.

tones and on the esters of oxalic acid, dimethylmalonic acid, succinic acid, tetralkylsuccinic acids, phthalic acids, etc. Furthermore, I shall attempt corresponding syntheses by means of acids of the types :



which are being made in this laboratory. I shall try to cause all these substances to rearrange into the corresponding α - and β -pinacolins.

In this connection I wish to call attention to an article by Dilthey and Last,¹ which appeared since my work commenced. They state that they obtain β -benzpinacolin (VI.), m. p. 182° , by the action of phenylmagnesium bromide on oxalic ester. I obtain, by this reaction, only pure benzpinacone, which melts at 186° – 187° , when heated alone or mixed with a portion of the substance made by another method. If β -benzpinacolin were formed in this reaction it would be in consequence of the rearrangement of the brommagnesium salt of benzpinacone (V.), which is produced by the action of the phenylmagnesium bromide on the oxalic ester.



The same salt (V.) is formed by the action of phenylmagnesium bromide on benzil, phenylbenzoin, benzilic ester and benzoylformic ester,² but from all these I have obtained only pure benzpinacone and never any β -benzpinacolin. As Dilthey and Last did not analyze their substance, I feel sure that they were dealing with impure benzpinacone.

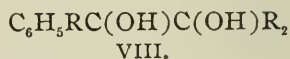
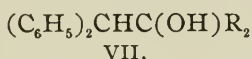
Experiments are being made to determine if these brommagnesium salts (V.), or the corresponding sodium salts, rearrange into the pinacolins. I have already obtained

¹ Ber. d. chem. Ges., **37**, 2639. This paper was written before I saw the recent articles of Valeur (Compt. rend., **132**, 833; **136**, 694; **139**, 480) and Dilthey and Last (Ber. d. chem. Ges., **37**, 3775).

² Acree : *Ibid.*, **37**, 2753.

β -benzpinacolin as one of the products formed by the distillation of the salt (V.) at about 400° .

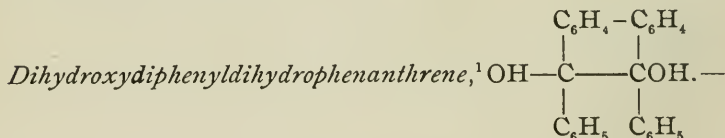
Diphenylacetic ester and benzoylformic ester are being used for the preparation of such substances as are represented by formulas VII. and VIII. I have also found that, by regulating the experimental conditions carefully, I can use Grignard's reagent, with advantage, to convert benzoylformic ester into dialkyl glycollic esters (IX.) :



The work outlined above will be continued.

EXPERIMENTAL.

Nearly all of the following work on the dihydroxydiphenyldihydrophenanthrene was completed in the University of Berlin before May 1, 1904 :



To a boiling solution of phenylmagnesium bromide (from 40 grams of brombenzene and 7 grams of magnesium turnings, in 50 cc. ether) 20 grams of phenanthrenequinone were gradually added. The solution was heated for three hours, cooled, poured into cold dilute sulphuric acid and shaken well. The ethereal extract was dried with sodium sulphate and the ether distilled. The residue of dihydroxydiphenyldihydrophenanthrene, when crystallized from alcohol, weighed 25 grams. Proportionate yields were obtained from smaller quantities. The substance melts at 178° – 179° . Analysis :

0.1745 gram substance gave 0.5465 gram CO_2 and 0.0952 gram H_2O .

¹ Werner and Grob : Ber. d. chem. Ges., 37, 2902.

	Calculated for $C_{26}H_{20}O_2$.	Found.
C	85.67	85.41
H	5.55	6.06

When 1 gram of the above substance was boiled for thirty minutes, in 50cc. glacial acetic acid, containing 0.3 gram chromic acid and water subsequently added to the solution, a precipitate of 0.85 gram of *o*-dibenzoyldiphenyl¹ was obtained. This melted at 163°–165° and when recrystallized once from glacial acetic acid at 165°. Analysis :

0.1483 gram substance gave 0.4678 gram CO_2 and 0.0702 gram H_2O .

	Calculated for $C_{26}H_{18}O_2$.	Found
C	86.14	86.03
H	5.02	5.14

Diphenylphenanthrone,² $\begin{array}{c} C_6H_4 \text{---} CO \\ | \qquad \qquad | \\ C_6H_4 \text{---} C(C_6H_5)_2 \end{array}$.—Twenty grams

of the above pinacone were heated, under a return condenser, with 40 grams of acetyl chloride, during six hours. The acetyl chloride was distilled off and about 19 grams of the β -pinacolin were obtained. It melted at 195°–198° and, when crystallized once from glacial acetic acid, at 198°. This melting-point was not changed by repeated recrystallization from the same solvent (Werner and Grob give 194°–196°).

Two grams of the compound, in 100 cc. glacial acetic acid, were boiled with 0.4 gram chromic acid, for one-half hour, under a return condenser. Water was added to the solution and the precipitate was filtered. It weighed 1.85 grams, melted at 196°–198° and at 197°–198° when mixed with the pure pinacolin. This result shows that chromic acid does not easily oxidize the pinacolin and therefore makes it very improbable that the α -pinacolin formula (II.), suggested by Werner and Grob for this substance, is the correct one. Analysis :

¹ Werner and Grob : Ber. d. chem. Ges., 37, 2902.

² Werner and Grob : Loc. cit.

0.1647 gram substance gave 0.5410 gram CO_2 and 0.0796 gram H_2O .

	Calculated for $\text{C}_{26}\text{H}_{18}\text{O}$.	Found.
C	90.12	89.58
H	5.25	5.37

Diphenylmethyl-o,o-phenylbenzoic Acid,

$(\text{C}_6\text{H}_5)_2\text{CHC}_6\text{H}_4\text{C}_6\text{H}_4\text{COOH}$.—Two grams of the above pinacolin were dissolved in 50 cc. ethyl alcohol, containing 10 grams of potassium hydroxide and the mixture heated in a sealed tube at 150° – 190° during six hours. The tube was opened and the precipitated potassium salt filtered through asbestos and dissolved in hot water. On acidifying with dilute sulphuric acid the organic acid precipitated; it weighed 1.7 grams and melted at 180° – 190° . When 0.20 gram was heated in 1 cc. alcohol, at 180° – 190° , in a sealed tube, during twelve hours, it was not changed. Titration indicates a monobasic acid. It very probably has the formula assigned above and not the isomeric structure,



I shall try to ascertain this by other syntheses.

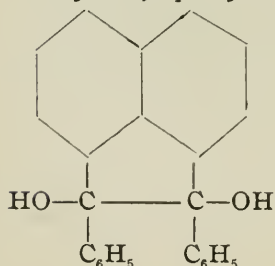
Titration.—(1) 0.1660 gram required 4.50 cc. $\text{N}/10$ KOH (phenolphthalein); calculated, 4.56 cc. (2) 0.1560 gram (heated at 190°) required 4.20 cc. $\text{N}/10$ KOH ; calculated, 4.28 cc.

Analysis :

0.1500 gram substance gave 0.4708 gram CO_2 and 0.0768 gram H_2O .

	Calculated for $\text{C}_{26}\text{H}_{20}\text{O}_2$.	Found.
C	85.66	85.60
H	5.55	5.69

Dihydroxydiphenyldihydroacenaphthene,



.—The acenaphthenequinone used in

this work was prepared according to Graebe's¹ method. A yield of 30 grams from 100 grams of acenaphthene was obtained. Fifteen grams of acenaphthenequinone were added, gradually, to a solution of phenylmagnesium bromide (from 40 grams brombenzene and 7 grams magnesium turnings, in 50 cc. ether). The substance dissolved completely and, after the solution had been boiled during two hours, the brommagnesium salt of the above compound was precipitated. The ether solution, after treatment with dilute sulphuric acid, was well shaken, dried with anhydrous sodium sulphate; the ether distilled and the residue crystallized from alcohol and from glacial acetic acid. The substance melted at 154°. When heated for some time with acetyl chloride, in a reflux apparatus, no change was apparent. Analysis :

0.1300 gram substance gave 0.4036 gram CO₂ and 0.0656 gram H₂O.

	Calculated for C ₂₄ H ₁₈ O ₂ .	Found.
C	85.16	84.67
H	5.38	5.60

Sym. Diphenyldi-p-tolylpinacone,

(C₇H₇)(C₆H₅)C—C(C₆H₅)(C₇H₇).—This is most readily pre-
OH OH

pared in the following manner :² The method will be employed for the formation of the corresponding *o*- and *m*-tolyl derivatives and other homologues.

Eight grams of benzil were added, gradually, to a boiling ethereal solution of *p*-tolylmagnesium bromide (from 20 grams of *p*-bromtoluene and 4 grams of magnesium turnings, in ether) and the solution boiled three hours. The mixture was poured into cold, dilute sulphuric acid, shaken well and the ether extract dried with anhydrous sodium sulphate. The ether was distilled and the residue taken up with a small amount of cold, absolute alcohol. In two days the pinacone was completely precipitated. It was recrystallized once from a little absolute alcohol and melted at 163°–165°. Yield,

¹ Ann. Chem. (Liebig), 276, 4.

² Acree : Ber. d. chem. Ges., 37, 2762.

10.4 grams. With sulphuric acid it gives a dirty-violet color. Analysis:

0.1730 gram substance gave 0.5387 gram CO_2 and 0.1043 gram H_2O .

	Calculated for $\text{C}_{28}\text{H}_{26}\text{O}_2$.	Found.
C	85.22	84.93
H	6.66	6.70

β -Di-*p*-tolylldiphenylpinacolin(?), $(\text{C}_7\text{H}_7)_2(\text{C}_6\text{H}_5)\text{C}-\text{COC}_6\text{H}_5$.—This was obtained by boiling the pinacone (6 grams) with acetyl chloride, during ten hours. It was crystallized three times from absolute alcohol and proved to be identical with Thörner's¹ compound, prepared by the interaction of *p*-tolylphenyl ketone and zinc, in concentrated alcoholic hydrochloric acid solution. The yield was 5.5 grams. The pinacolins obtained by both methods and also a mixture of the two, melted at 136° . Analysis:

0.1529 gram substance gave 0.4998 gram CO_2 and 0.0928 gram H_2O .

	Calculated for $\text{C}_{28}\text{H}_{24}\text{O}$.	Found.
C	89.31	89.15
H	6.44	6.74

Action of Phenylmagnesium Bromide on Ethyl Oxalate.

Benzpinacone.—This substance was made to ascertain with what ease such glycols could be prepared from the esters of dibasic acids. As pointed out in the introduction, the work will be continued on a large number of aliphatic dibasic acids and the related hydroxy acids.

Dilthey and Last² state that only β -benzpinacolin, m. p. 182° , is formed by this reaction. I obtain pure benzpinacone.

To phenylmagnesium bromide (from 40 grams brombenzene and 10 grams magnesium turnings) ethyl oxalate (8 grams) was added slowly; both were in absolute ethereal solution. The mixture was boiled one hour in a reflux apparatus, then poured into cold, dilute sulphuric acid, well

¹ Ann. Chem. (Liebig), 189, 110.

² Ber. d. chem. Ges., 37, 2639.

shaken, the ethereal layer dried with calcium chloride, the ether distilled and the residue crystallized from alcohol. Pure benzpinacone (12 grams), melting at 186° – 187° , was obtained. When a specimen of this was mixed with one of benzpinacone, prepared from methyl benzsilicate and phenylmagnesium bromide,¹ the melting-point was unchanged.

As Dilthey and Last did not analyze their compound, it seems probable that it consisted of impure benzpinacone, because even a small amount of impurity lowers the melting-point of this substance considerably.

It was very important to determine if the normal compound (pinacone), or the rearranged substance (pinacolin), is the first product of the action of Grignard's reagent on the esters of these dibasic acids, for it is very probable, indeed nearly certain, from work that will be described below, that the substances obtained from succinic and glutaric esters and their homologues, eliminate water very readily and form inner anhydrides—derivatives of tetramethylene and pentamethylene oxides. Analysis :

0.1358 gram substance gave 0.4236 gram CO_2 and 0.0790 gram H_2O .

	Calculated for $\text{C}_{26}\text{H}_{22}\text{O}_2$	Found.
C	85.20	85.07
H	6.07	6.46

Action of Phenylmagnesium Bromide on Ethyl Succinate.

Tetraphenyltetramethylene Glycol,
 $(\text{C}_6\text{H}_5)_2\underset{\text{OH}}{\text{C}}\text{CH}_2\text{CH}_2\text{—}\underset{\text{OH}}{\text{C}}(\text{C}_6\text{H}_5)_2$.—This substance was prepared

in the same manner as the benzpinacone. I have nothing to add to its properties, as described by Dilthey and Last,² except that my specimen melted at 206° instead of 202° .

Ten grams of ethyl succinate, in absolute ether, were added, gradually to a similar solution of phenylmagnesium bromide (from 40 grams of brombenzene and 7 grams of magnesium turnings), which was cooled in ice. The solution was allowed to stand

¹ Acree: Ber. d. chem. Ges., 37, 2761.

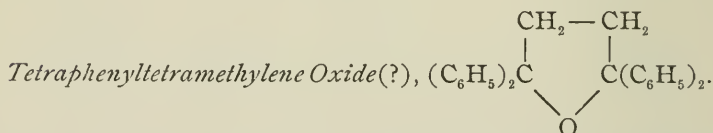
² Loc. cit.

see notes p 647.

several hours and was then poured slowly into a separatory-funnel containing finely divided ice. After thorough shaking, just enough dilute sulphuric acid was added to dissolve the magnesium hydroxide. The aqueous solution was removed and the cold ether layer filtered from the precipitated glycol. When dried and evaporated, the ethereal filtrate yields a residue containing more of the glycol. The latter is always accompanied by a substance, m. p. 163° – 165° , formed by the loss of 1 molecule of water from a molecule of the glycol. When a mixture of the two is crystallized from acetone, the glycol is readily obtained pure, but two or three crystallizations of the mixture from boiling glacial acetic acid are sufficient to convert it completely into the anhydride. The same result is obtained by boiling the glycol for a short time with acetyl chloride. The pure glycol melts at 206° . Analysis :

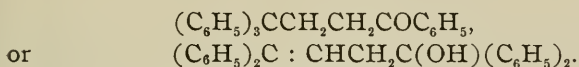
0.1539 gram substance gave 0.4775 gram CO_2 and 0.0945 gram H_2O .

	Calculated for $\text{C}_{28}\text{H}_{26}\text{O}_2$.	Found.
C	85.22	84.62
H	6.66	6.82



—This is the only substance formed when ethyl succinate is treated with boiling solution of phenylmagnesium bromide and the product purified at ordinary temperatures, without any special precautions. It is also formed when the above glycol is boiled for only a few minutes with acetyl chloride and then crystallized from glacial acetic acid. It crystallizes best from alcohol and melts at 163° – 165° . Mixtures of specimens prepared by various methods melt at the same temperature.

The above formula is offered tentatively, as the substance might be the β -pinacolin corresponding to the tetraphenyl-tetramethylene oxide,

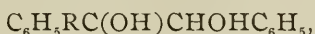


It only slowly decolorizes bromine, in chloroform solution. Experiments are in progress to definitely establish its constitution. Analysis:

0.1875 gram substance gave 0.6156 gram CO_2 and 0.1071 gram H_2O .

	Calculated for $\text{C}_{28}\text{H}_{24}\text{O}_2$.	Found.
C	89.35	89.54
H	6.44	6.36

Diphenyl Ethyl Glycol, $\text{C}_6\text{H}_5(\text{C}_2\text{H}_5)\text{C}(\text{OH})\text{CHOHC}_6\text{H}_5$.—It has been shown¹ that the aryl magnesium bromides react very readily with benzoin to give the diphenyl aryl glycols,



which were previously only obtained with difficulty. I am now extending this reaction to the corresponding diphenyl aliphyl glycols.

Ethyl iodide (20 grams) and magnesium turnings (4 grams), were boiled in ether till the magnesium was no longer dissolved. Benzoin (12 grams) was then added gradually to the boiling solution. When the reaction was complete, the liquid was poured into cold, dilute sulphuric acid and shaken well. The ether solution was dried, distilled and the residue crystallized from 50 per cent alcohol. The product weighed 13 grams and melted at about 110° . When crystallized from carbon disulphide it melts at 115° – 116° . The substance is attacked only very slowly by bromine, in chloroform solution. Analysis:

0.1801 gram substance gave 0.5233 gram CO_2 and 0.1210 gram H_2O .

	Calculated for $\text{C}_{16}\text{H}_{18}\text{O}_2$.	Found.
C	79.27	79.25
H	7.50	7.46

m-Tolyldiphenylcarbinol, $\text{C}_7\text{H}_7(\text{C}_6\text{H}_5)_2\text{COH}$. — This com-

¹ Acree : Ber. d. chem. Ges., 37, 2762.

pound and also the methane derivatives described below, had been prepared before the publication of an article by Bistrzycki and Gyr,¹ but this is the first opportunity I have had to publish my results. I also desire to state that, unfortunately, I had overlooked Herzig and Wengraf's² work, when I described my method for the reduction of carbinols to methane derivatives. The two methods are entirely different and I applied mine to the reduction of halogen compounds, hence both will certainly be useful.

No description of the conditions for obtaining ethyl *m*-toluate in good yield appears in the literature. I give the one I have used. *m*-Toluic acid (15 grams) was dissolved in absolute ethyl alcohol (100cc.) and concentrated sulphuric acid (11 grams) was added. The mixture was boiled four hours; nearly two-thirds of the alcohol was then distilled off, water and excess of sodium carbonate were added and the precipitated oily ester was separated, dissolved in ether, dried with anhydrous sodium sulphate and distilled. Besides the first fraction, 16 grams, or 88.4 per cent of the theoretical, consisted of pure ester, boiling at 234° to 235°, 762 mm.

Ethyl *m*-toluate (17 grams), in ether, was added to a similar solution of phenylmagnesium bromide (from 40 grams of brombenzene and 7 grams of magnesium turnings). After boiling three hours, the liquid was poured into cold, dilute sulphuric acid, shaken well, the ethereal extract dried with sodium sulphate, the ether distilled and the residue fractionated. A first fraction of diphenyl (1.2 grams) was obtained, which melted at 69°. The *m*-tolylidiphenylcarbinol boiled at 255° (26 mm.). When this was crystallized from ligroin three times, 5.3 grams of carbinol melting at 65° were obtained. The melting-point was not lowered when the substance was mixed with a sample prepared by another method.³ Analysis :

¹ Ber. d. chem. Ges., **37**, 1245.

² Monats. Chem., **22**, 613.

³ Acree : Ber. d. chem. Ges., **37**, 993; Bistrzycki and Gyr : *Ibid.*, **37**, 1250.

0.1610 gram substance gave 0.5170 gram CO_2 and 0.1022 gram H_2O .

	Calculated for $\text{C}_{20}\text{H}_{18}\text{O}$.	Found.
C	87.52	87.58
H	6.63	7.05

Reduction of m-Tolyldiphenylcarbinol to m-Tolyldiphenylmethane.—The carbinol (2 grams) was boiled with tin (10 grams) and alcohol (50 cc.), in a reflux apparatus, concentrated hydrochloric acid (15 cc.) was added gradually, during about six hours. The solution was poured into water and the precipitated methane derivative distilled; 1.3 grams, boiling at 220° – 250° (30 mm.), were obtained. It first melted at 59° , but, when crystallized from ligroin, at 62° . The substance is identical with a specimen kindly furnished me by Professor Bistrzycki.¹ Analysis:

0.1537 gram substance gave 0.5232 gram CO_2 and 0.1005 gram H_2O .

	Calculated for $\text{C}_{20}\text{H}_{18}$.	Found.
C	92.96	92.84
H	7.04	7.26

Reduction of o-Tolyldiphenylcarbinol to o-Tolyldiphenylmethane.—This was effected exactly as in the case of the *meta*-compound. Two grams of the carbinol gave 1.5 grams of methane derivative, which melted at 78° and 80° , after crystallization from alcohol and ligroin, respectively. The substance is identical with a specimen kindly furnished me by Professor Bistrzycki.² Analysis:

0.1623 gram substance gave 0.5520 gram CO_2 and 0.1051 gram H_2O .

	Calculated for $\text{C}_{20}\text{H}_{18}$.	Found.
C	92.96	92.76
H	7.04	7.19

¹ Bistrzycki and Gyr: Ber. d. chem. Ges., **37**, 1251.

² *Loc. cit.*

OBITUARY.

THOMAS MESSINGER DROWN.

President T. M. Drown, who died at his home, South Bethlehem, Pa., November 15, 1904, was born March 19, 1842. He attended the Philadelphia High School and graduated M.D., from the University of Pennsylvania, in 1862. After a short period of medical practice, he studied chemistry at the Universities of Yale, Harvard and Heidelberg and at the School of Mines, Freiberg, Saxony. During several years he was an analytical chemist in Philadelphia, then, successively, professor of chemistry at Lafayette College, Easton, Pa., 1874-'81 and at the Massachusetts Institute of Technology, 1885-'95. He was secretary of the American Institute of Mining Engineers, 1873-'83 and president 1897-'98. Since 1887 he had been in charge of the Chemical Department of the Massachusetts State Board of Health. He was appointed president of Lehigh University in 1895 and received the degree of LL.D. from Columbia University the same year. Dr. Drown was the author of numerous papers on metallurgical, sanitary and analytical chemistry, several of which were published in the earlier volumes of *THIS JOURNAL*, but these fail to represent adequately his services to science in general and to chemistry in particular. His lofty ideals, combined with unusual ability and skill, were important factors in giving Massachusetts its present leadership in sanitary matters and in laying the foundations for the high standards of work which prevail at the Institute of Technology. The editor desires to make special mention of the charm of Dr. Drown's personality. This, together with his unerring instinct for the highest and best in professional affairs, made intercourse with him an unalloyed pleasure.

ISAAC LOWTHIAN BELL.

Sir Lowthian Bell, Bart., the veteran iron master and metallurgist, was born Feb. 15, 1816, at Newcastle and died, in his 90th year, at Northallerton (England), Dec. 20, 1904. He studied at Edinburgh University and the Sorbonne and entered his father's iron works at the age of 24. In 1850 he became connected with a chemical factory at Washington (England); this he greatly enlarged and laid down an extensive plant for the manufacture of a lead oxychloride, introduced as a substitute for white lead by his father-in-law, Mr. H. L. Pattinson, F.R.S., who was associated with him in the busi-

ness. The production of aluminium, by the Deville sodium process, was also carried on at the works from 1860. Sir Lowthian Bell is, perhaps, best known for the highly successful iron works which he started at Port Clarence, to work the Cleveland ore, soon after its discovery in 1850. The degree of LL.D. was conferred on him by Edinburgh University in 1893, he was made a baronet in 1885, received the first Bessemer gold medal in 1874 and during the same year became a Fellow of the Royal Society. One of the founders of the "Iron and Steel Institute," Sir Lowthian Bell became president 1873-75; a number of other scientific societies in this country and in Europe also elected him to membership. He was the author of "Principles of Iron and Steel Manufacture," "The Chemical Phenomena of Iron Smelting" and of many papers on the same subjects published in various scientific and technical journals.

ABBREVIATIONS.

The following abbreviations will be used for citations in
THIS JOURNAL:

THIS JOURNAL	for	American Chemical Journal.
Am. J. Sci.	"	American Journal of Science.
Ann. Chem. (Liebig)	"	Justus Liebig's Annalen der Chemie.
Ann. Chim. Phys.	"	Annales de Chimie et de Physique.
Ber. d. chem. Ges.	"	Berichte der deutschen chemischen Gesellschaft.
Bull. Soc. Chim.	"	Bulletin de la Société Chimique de Paris.
Chem. News	"	Chemical News.
Chem. Ztg.	"	Chemiker-Zeitung.
Centrabl.	"	Chemisches Central-Blatt.
Compt. rend.	"	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences (Paris).
Gazz. chim. ital.	"	Gazzetta chimica italiana.
Jahres. d. Chem.	"	Jahresberichte der Chemie.
J. Am. Chem. Soc.	"	Journal of the American Chemical Society.

J. f. Chem. Physik.	for Journal für Chemie und Physik.
J. Chim. Phys.	“ Journal de Chimie Physique.
J. Chem. Soc.	“ Journal of the Chemical Society (London).
J. Physic. Chem.	“ Journal of Physical Chemistry.
J. prakt. Chem.	“ Journal für praktische Chemie.
J. Soc. Chem. Ind.	“ Journal of the Society of Chemical Industry.
Monats. Chem.	“ Monatshefte für Chemie.
Phil. Mag.	“ Philosophical Magazine.
Phil. Trans.	“ Philosophical Transactions of the Royal Society (London).
P. Am. Acad.	“ Proceedings of the American Academy of Sciences.
P. Chem. Soc.	“ Proceedings of the Chemical Society (London).
P. Roy. Soc.	“ Proceedings of the Royal Society (London).
Rec. Trav. Chim.	“ Recueil des Travaux Chimiques des Pays-Bas.
Sitzun. Wien.	“ Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften (Wien).
Z. anal. Chem.	“ Zeitschrift für analytische Chemie.
Z. ang. Chem.	“ Zeitschrift für angewandte Chemie.
Z. anorg. Chem.	“ Zeitschrift für anorganische Chemie.
Z. Chem.	“ Zeitschrift für Chemie.
Z. Elek. Chem.	“ “ “ Elektrochemie.
Z. physiol. Chem.	“ “ “ physiologische Chemie.
Z. physik. Chem.	“ Zeitschrift für physikalische Chemie.

REVIEWS.

JAHRBUCH DER ELEKTROCHEMIE. Berichte über die Fortschritte des Jahres 1902. Herausgegeben von DR. HEINRICH DANNEEL, Privatdocent der physikalischen Chemie und der Elektrochemie an der Technischen Hochschule zu Aachen. IX Jahrgang. Halle, a. S.: Verlag von Wilhelm Knapp. 1904. pp. 750. Price, M. 24.

The "Jahrbuch der Elektrochemie," as is well known, reviews the work of the year under the two general heads of "scientific" and "applied" electrochemistry. The scientific portion includes a discussion of conductivity and solutions, chemical energy and electrical energy, polarization and electrolysis and electrical phenomena in gases. The applied electrochemistry deals with production of current, inorganic electrochemical procedure and products, metals, organic compounds, alkali electrolysis and a discussion of apparatus for technical electrochemistry.

The volume in question is very rich in material and the abstracts, on the whole, seem to have been carefully prepared.

H. C. J.

KRITISCHE STUDIEN ÜBER DIE VORGÄNGE DER AUTOXYDATION. Von C. ENGLER und J. WEISSBERG. Braunschweig: Friedrich Vieweg und Sohn. 1904. pp. xi + 204.

A Review of a Book and a Theory.

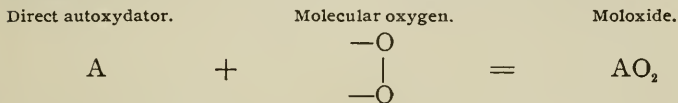
The dedication of this recent publication on oxidation processes to the memory of Christian Friedrich Schönbein, is certainly a mark of thoughtful appreciation on the part of the authors, while the book itself is a "Denkmal" not unworthy of the genius of this brilliant observer. As its title indicates, it has for its object the discussion and elucidation of all problems connected with autoxidation. The authors are careful to point out that the key to an understanding of all processes of oxidation is to be found in the writings of Schönbein, whose words upon this subject seem to us, after a lapse of more than fifty years, to be well nigh prophetic. According to this distinguished observer we see, in the final products of chemical combinations, particularly those in which oxygen is concerned, only the closing scene, as it were, of a chemical drama, which in reality consists of several acts. Beginning with the labors of Schönbein and extending down to the present, it has been the aim of a certain school of chemists to better portray the beginning and middle, as well as the final acts of the oxygen drama; a part of the object of the publication here under consideration is to show how well they have succeeded. The writer believes, as doubtless also do the authors, that the opin-

ions and researches described in this book form a distinct period in the growth and development of our chemical knowledge.

Such being the case, it may not be out of place to give a brief summary of the origin and development of the modern theory of oxidation, particularly for the benefit of those whose work and reading have been more or less remote from the subjects here under consideration.

When we consider the remarkably perfect shape in which the great Lavoisier left the oxygen theory of combustion, in spite of his untimely death, the vast amount of knowledge concerning oxidation phenomena that has accumulated since his time is all the more notable; it certainly bodes ill for the lasting triumph of any of our pet theories that as nearly perfect, far-reaching and revolutionary as were Lavoisier's conceptions of oxidation processes, they should fall so far short of the views that prevail to-day. As is pointed out in the book before us, it was the discovery by Schönbein, in 1840, of ozone and the recognition of its formation during slow oxidations, that gave the first impulse to a deeper inquiry into the causes and mechanism of such reactions. This, together with the discovery of the equally remarkable substance, hydrogen peroxide and the detection of it among the final products of such autoxidations as were brought about in the presence of water, were the starting-points for the extended investigations of Schönbein, Moritz Traube, Engler, Bach, Manchot and others in this field of research. Their work has brought to light many new and interesting facts and gradually the results have been elaborated into a general theory of oxidation phenomena, so comprehensive in its scope as to include nearly every possible phase of the processes. It is hardly feasible to give anything like a satisfactory outline of this theory in a limited space. Briefly, however, it is based upon the conception of partial dissociation both of the oxygen molecule and of that of the oxidizable material, whereby the former becomes free to combine with the autoxidizable substance. To Moritz Traube we owe the conception that, in slow oxidations, it is the molecule of oxygen rather than the atom that participates in the change. Thus combination of the oxygen molecule with the autoxidizable substance leads to the formation of peroxides. These compounds have been called *holoxides* by Traube, *moloxydes* by Engler and *primary oxides* by Manchot. The ultimate fate of these compounds depends largely on the composition and nature of the other substances (acceptors) with which they find themselves in contact. In the light of this theory the formation of peroxides, of ozone and hydrogen per-

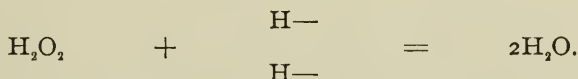
oxide and ultimately of simple oxides, as products of autoxidation, all becomes readily intelligible ; it also takes cognizance of the difference between direct and indirect autoxidation. Graphically these ideas have been expressed as follows :



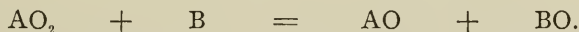
Examples of such oxidations are to be found in the autoxidation of hydrogen, the alkali metals and benzaldehyde ; thus on burning rubidium in air it is quantitatively transformed into the peroxide and, as pointed out by Schuller and later by Traube, the flame of burning hydrogen contains hydrogen peroxide. If the acceptor be the same as the autoxidizable substance, the final product of the oxidation will be a single simple oxide. Thus it is that water is the final oxidation-product of hydrogen ; in terms of the theory, this is represented graphically as follows :



and



In the event that the acceptor is different from the autoxidator, two substances may be ultimately oxidized as the result of the autoxidation of the first which will then act in the capacity of an oxygen carrier to the second, thus we should have :



An example of this is found in the oxidation of sodium arsenite by means of sodium sulphite, as a carrier :

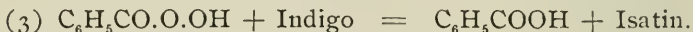
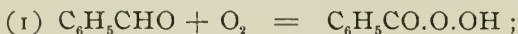


and



The oxidation of benzaldehyde by atmospheric oxygen, at ordinary temperatures, furnishes an admirable example. As pointed out by Baeyer and Villiger, on autoxidation, the aldehyde is first converted into benzoyl hydroperoxide ; if this be

allowed to react with a molecule of the aldehyde, it forms two molecules of benzoic acid, but, if another readily oxidizable substance, such as indigo, be present this is oxidized and only one molecule of benzoic acid is produced. These changes may be represented graphically as follows :

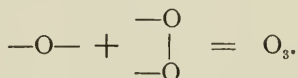


The increase in reactivity of oxygen is explained by the formation of the active peroxide, as the result of the action of the oxygen of the air upon the aldehyde. In reaction (2) the benzaldehyde behaves as a self-acceptor, whereas in reaction (3) indigo is the acceptor.

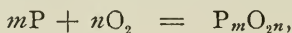
The theory also enables us to understand the formation of ozone, by the action of electricity on ordinary oxygen and as the result of slow oxidations ; in the first case molecular oxygen is both partially and completely dissociated :



and



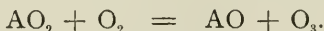
In the second case the ozone is supposed to be a decomposition-product of the moloxide resulting from the autoxidation ; thus, according to Ostwald, in the slow oxidation of phosphorus the changes are represented by the equations :



and

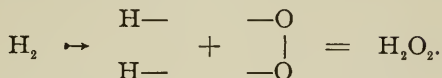


Thirdly, oxygen may act as the acceptor in certain oxidations :

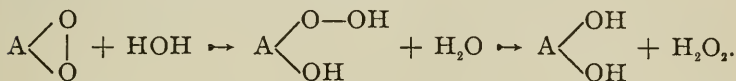


The third point with which the theory concerns itself is the formation of hydrogen peroxide. As already mentioned above, this compound is the primary product in the oxidation of hydrogen, being present, according to Traube, in the flame of burning hydrogen and also resulting from the action of molecular oxygen on cathode hydrogen, but it is never formed in the reverse way, *viz.*, by the action of molecular hydrogen on atomic oxygen. These are certainly most interesting and

important observations from the standpoint of the theory and may be formulated as follows :

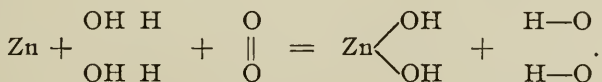


Secondly, as pointed out by Engler, hydrogen peroxide may be produced in processes of oxidation as the result of secondary reactions. Thus it may result from the decomposition of another peroxide by means of water :



According to Engler, the oxidation of turpentine results in the formation of hydrogen peroxide as a secondary product.

Thirdly, Schönbein observed that hydrogen peroxide is formed in a very large number of oxidations which take place in the presence of water ; in explanation of this, he suggested that one atom of the oxygen molecule formed the *ozonide*, whereas the other, oppositely charged atom, oxidized water with the production of hydrogen peroxide, which he regarded as an *autozonide*. Later, very similar views were advanced by Hoppe-Seyler, who considers that the autoxidizable substance decomposes an oxygen molecule and appropriates one atom itself, leaving the other in the form of active, nascent oxygen, which has the power of causing energetic oxidations, such as that of molecular oxygen to ozone, of ammonia to nitrite and of water to hydrogen peroxide. According to Traube, the formation of hydrogen peroxide as a by-product in such autoxidations as may be effected in the presence of water, depends rather on the more ready decomposition of the water molecule and the oxidation of the resulting nascent hydrogen by molecular oxygen. He represents the formation of hydrogen peroxide, as the result of the autoxidation of zinc in contact with water, by the equation :

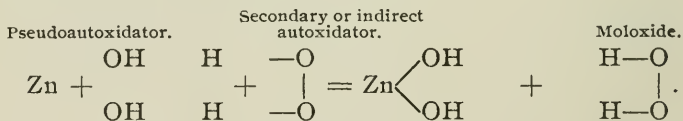


In support of this conception he pointed out that, whereas the alkali metals readily decompose water, they retain their luster in dry oxygen, sodium, for example, after remaining bright during forty hours, became covered with a layer of the hydroxide the moment a trace of water was admitted. That water is the active agent in such oxidations is also shown by

the fact that, when shaken with oxygen and absolute alcohol, zinc is not oxidized nor is hydrogen peroxide produced. He also concluded that, although pure zinc alone cannot decompose either oxygen or water molecules, it does combine with the oxygen atom in water when assisted by the affinity of molecular oxygen for the hydrogen atoms of water, which is exerted in the opposite sense.

In view of the simplicity and beauty of these conceptions, it is not surprising that Traube should have been led to magnify, somewhat, the part played by water in processes of autoxidation and, contrary to his earlier notions, should have held the extreme view that, at ordinary temperatures, no oxidation can take place in the absence of water. While, perhaps, such a generalization is too sweeping, it is interesting to note, in passing, that all later researches on the influence of water on chemical combination have tended, in large measure, to confirm it.

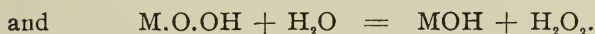
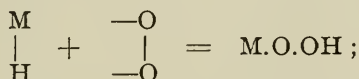
So far as I am able to determine, the labors of Engler, Bach, Manchot and their co-workers in this field have consisted largely in the extension and elaboration of the views of Traube and in the adjustment and adaptation of them to modern chemical conceptions. Thus, in the autoxidation of zinc in the presence of water, Engler regards the zinc as a pseudoautoxidator, which gives rise to atomic hydrogen; this latter, regarded by him as a second or indirect autoxidator, is the substance which really combines with the oxygen of the air. Graphically these changes are represented thus:



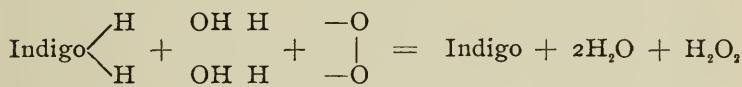
This mode of representation is essentially similar to Traube's given above.

A still further development of the theory by Engler and Weissberg is based upon the supposition that the metals pass into solution, in the form of positively charged ions, in consequence of their solution tension; these, however, can only be discharged and enter into chemical combination at the expense of the hydroxyl ions of water, but this involves the discharge of a corresponding number of hydrogen ions, which become atomic and at once combine with molecular oxygen to form hydrogen peroxide, just as, in Traube's experiment, the atomic hydrogen, liberated at the cathode, unites with molecular oxygen to form hydrogen peroxide. These authors are also disposed

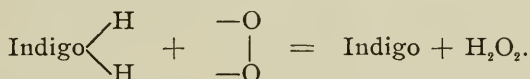
to the view that atomic hydrogen, resulting from the discharge of hydrogen ions by combination of metallic ions with hydroxyl ions of water, unites with the remainder of the metal, or is absorbed by it, in much the same way that hydrogen is absorbed by palladium. A secondary autoxidator, of the composition MH , is thus produced which combines with molecular oxygen to form a hydroperoxide of the form $M.O.OH$; this, in contact with water, at once yields the hydroxide of the metal and hydrogen peroxide:



The autoxidation of indigo white in presence of water is an ionic reaction, like the oxidation of a metal under similar conditions, therefore, these authors are inclined to represent it by the formula:



rather than by the shorter one,



They have also pointed out that Traube's theorem, that no oxidation occurs at ordinary temperatures in the absence of water, is not generally valid and that the hydrogen peroxide, formed in certain oxidations, is not to be regarded as a primary, but rather as a secondary product, resulting from the decomposition, by water, of the moloxide first formed in the oxidation. Thus, in the production of hydrogen peroxide by the oxidation of turpentine in moist air, they believe that the turpentine and molecular oxygen form a peroxide, which yields hydrogen peroxide with water.

Accordingly, Engler and his co-workers distinguish between (1) reactions in which hydrogen peroxide is produced directly by the autoxidation of hydrogen, or of something producing it: this includes free hydrogen, cathode hydrogen, hydrogen from zinc and water, labile hydrogen of certain organic compounds etc. and (2) reactions in which the directly autoxidizable body is a substance quite different from hydrogen, such as turpentine,

triethyl phosphine, dry metals, etc., from these, hydrogen peroxide is only formed indirectly and as the result of a secondary process, *viz.*, the decomposition of the given moloxide by water. Engler and Weissberg are responsible for the concept "no oxidation without dissociation," in support of which they cite the fact that turpentine and certain essential oils can be kept in the dark, for a very long time, without oxidation.

Similarly hydrogen, which at high temperatures combines explosively with oxygen, scarcely combines with it at all at ordinary temperatures, whereas dissociated hydrogen, *i. e.*, cathode hydrogen and nascent hydrogen, combines rapidly with molecular oxygen at ordinary temperatures. Dissociation is used to signify the setting free of valencies in the compound or element undergoing oxidation and the partial liberation of the valencies in the oxygen molecule. As Thiele regards the partial valencies of unsaturated compounds as the cause of their formation of addition-products, so Engler believes that the reason for combination with oxygen consists in the loosening of combined valencies in the element or compound by heat, light, or other cause. In support of this conception the authors point out that many substances which are very readily oxidized also exhibit a strong tendency to polymerize, this is partially true of styrene and its derivatives, also of indene, cumarone and certain hydrocarbons of the petroleum series. The authors attribute this tendency to polymerization to the same cause as the tendency to oxidation, *viz.*, to the existence of unsaturated valencies in the molecules.

The closing chapter of the book deals with the rôle of oxygen in the living organism, it is in this direction that the newer theories of oxidation have found a most interesting and important application and to Bach, especially, belongs the credit of having been the first to point out that the oxidizing ferments of the blood are simply readily oxidizable substances, having a special aptitude to form peroxides. Kastle and Loevenhart subsequently showed the many analogies existing between organic peroxides and the oxidizing ferment of the potato and indicated that, in all probability, this substance is not a true soluble ferment, but simply a very unstable organic peroxide and that the living cell apparently renders oxygen reactive in essentially the same way as does phosphorus, benzaldehyde and other oxygen carriers, as one phase of autoxidation.

* * * * *

In the book itself most of the ideas here touched upon are elaborated with great clearness and illustrated by abundant references to the original literature. In my opinion its publication

will prove to be one of the milestones along the way of chemical progress. Compared with the great lessons which it teaches, its imperfections sink into comparative insignificance. There are, however, a few omissions in the literature of the subject which have come under my observation; under phosphorus no reference is made to the splendid researches of Thorpe and Tutton,¹ on the slow oxidation of phosphorus and yet, in point of thoroughness, their investigations far surpass all other work on this subject and incidentally, as may be pointed out in the future, throw a great deal of light on Schönbein's old observation, subsequently much discussed and investigated, that one atom of oxygen is rendered reactive by every two atoms of phosphorus oxidized.

Also, throughout the book, there is a hair-splitting accuracy as to the date of publication of many of Engler's own contributions to the subject, which is bound to impress the dispassionate and unbiased reader disagreeably and which is of no interest to any one except, perhaps, to those engaged in establishing far-reaching claims of priority. One cannot get away from the notion that there must exist some apprehension in the minds of the authors lest the chemical world may, perchance, allow its gaze to wander past the heroic figure of Engler to the humbler personages of Bach and Manchot, or perhaps, even more remotely, to Moritz Traube. It is sometimes refreshing to think that John Dalton was actually so occupied with his investigations, that he probably never knew just precisely what and how much had been contributed to our knowledge of the expansion of gases by heat, by Gay-Lussac, Charles, himself and others. Concerning the remarkable activity in this field of research at that time, he simply says that "The truth will out at last" and yet, at the present, no one, not even a German chemist, is inclined to doubt that this great Manchester chemist, independently of every one else, arrived at many laws governing the conduct of gases.

Finally, were one disposed to be critical, both the originality and the correctness of the authors' conclusions respecting the function of catalase in the green plants, as set forth in bold type on page 191, might be questioned. The notion there advanced, presumably as original with the authors, is, in reality, but little more than a fusion of the views of Erlenmeyer and Loew; yet no mention is made of the views of the former chemist in this connection. When we recall that aqueous extracts of the liver of the hog, the testicle of the sheep and of the common edible mushroom, *Agarica campestris*, all decom-

¹ J. Chem. Soc., 1886, 833; 1890, 545, 573.

pose hydrogen peroxide far more actively than aqueous extracts of the chlorophyl-bearing plants, we do not feel quite so certain that catalase is merely an adjunct of the photosynthetic process.

J. H. KASTLE.

RADIO-ACTIVITY. By E. RUTHERFORD, D.Sc., F.R.S., F.R.S.E., MacDonald Professor of Physics, McGill University, Montreal. Cambridge University Press. 1904. pp. 399.

There are few subjects in any branch of experimental science that have produced more confusion than that of radioactivity. This is due, in part, to the large number of papers that have appeared in this field in the last few years and in part to the variety of subjects dealt with. There has also been a lack of any wide-reaching generalization, in terms of which the large number of apparently disconnected facts could be coordinated.

The whole subject has been greatly simplified by this admirable little book, which contains just those things that we wish to carry with us. Rutherford points out that the whole subject of radioactivity was opened up by the discovery of the X-rays. Investigations were made to see if anything analogous to this kind of radiation was given out by ordinary matter. The result was the discovery of the radioactivity of uranium, by Becquerel, in 1896; in 1898 Schmidt showed that thorium is also radioactive.

Mme. Curie determined the radioactivity of a number of minerals containing uranium and thorium and found some specimens of pitchblende that were four times as radioactive as metallic uranium. This led to the discovery of radium by M. and Mme. Curie, which, in the pure state, has a radioactivity that is more than *a million times* that of metallic uranium. Radium chloride comes from the pitchblende together with the barium chloride, which it closely resembles chemically and from which it is finally separated by difference in solubility in water and alcohol.

Other radioactive substances, such as polonium and actinium, have also been separated from pitchblende.

Several methods have been employed to *measure radioactivity*. They depend upon the power of the rays to affect a photographic plate, to produce fluorescence on a screen covered with barium platinocyanide, zinc sulphide, etc. and to ionize a gas. Methods based upon the ionizing power of the rays have now nearly supplanted all others, especially where quantitative measurements of radioactivity are to be made.

Rays of very different properties are given off by radioactive substances. This has been shown by observing their deflection in a magnetic field and by comparing their relative ab-

sorption by solids and gases. Three kinds of rays have been detected, known respectively as the α -, β - and γ -rays.

The α -rays are very readily absorbed by thin metal foil and by a few centimeters of air. They are deviated in a magnetic field in the opposite sense to the cathode rays and, as the latter are charged negatively, the α -rays must consist of positively charged particles. The conclusion, from this and other experimental evidence, is that the α -particle is positively charged, has a mass about twice that of the hydrogen atom and moves with a velocity of about one-tenth that of light.

The β -rays are far more penetrating than the α -rays. They carry a negative charge, are strongly deviated by a magnetic field and move with the velocity of light. These properties suggest the cathode rays in a vacuum-tube. In order to determine whether the two are identical, it is highly desirable to determine the ratio of the charge carried by the particle to its mass. Representing the charge by e and the mass by m , it is well known, from the work of J. J. Thomson, that for the

cathode particle $\frac{e}{m} = 10^7$. By observing the deviation in a magnetic field Becquerel showed that for the β -particle, $\frac{e}{m} = 10^7$, thus establishing the identity of the β -rays with the cathode rays.

The γ -rays are extremely penetrating, much more so indeed, than the X-rays produced in a high-vacuum tube. They are not deviated appreciably by a magnetic field. Although the nature of the γ -rays is not known, it can be said that they resemble, in many of their properties, very penetrating X-rays.

In addition to the three kinds of radiation described above, *radium is continually giving out heat energy in relatively large quantity.* This was shown in a number of ways. Radium bromide was found to maintain itself at a temperature above that of the surrounding medium; it was found to liquefy continuously the ice in an ice calorimeter, thus permitting the determination of the rate at which it gave out heat. It was shown that *1 gram of pure radium emits about 100 calories of heat per hour.*

The interesting and important question in this connection is, what is the source of the comparatively large amount of energy that is being continually given out by radium? When the fact was first discovered, there was a tendency on the part of some to rush to the conclusion that the law of the conservation of energy had been overthrown, but those with scientific minds

looked about for an explanation of this remarkable and unique fact. At least two possible theories have been proposed. One is that, as the α -particles are absorbed in a thickness of radium of less than 0.001 cm., most of them would be stopped in the radium itself and their energy of motion would be manifested in the form of heat. This, however, would not account for all the heat emitted by radium.

Another theory is that the radium atom is undergoing contraction analogous to the sun and is, therefore, liberating heat energy.

In addition to the three kinds of rays described above and to the heat energy, radium and other radioactive substances give off an *emanation*, with distinctive and certain very remarkable properties. The emanation is driven out of salts of radium at an elevated temperature and is *produced in these salts after a time*. It can be condensed by immersing the tube through which it is passed in liquid air. It condenses at from -150° to -155° . Probably because such a small quantity of the emanation can be obtained, nothing is visible in the tube at the place where condensation occurs, except that the glass becomes fluorescent at this point. The emanation thus resembles a gas. Rutherford has determined the rate at which it diffuses and from this has calculated its approximate molecular weight to be about 100. The emanation is, therefore, not radium itself, as the latter has an atomic weight of at least 225 and probably higher.

The emanation given off by radium and other radioactive substances is *unstable*. It is itself highly radioactive and is the chief source of the heat liberated by radium. Its most remarkable property, however, is that *it yields helium as one of its decomposition-products*. This was established by Sir William Ramsay and Mr. Soddy and has subsequently been confirmed by others. *This is the first authentic example on record of one elementary form of matter being produced from another.*

Several *theories* have been proposed to account for radioactivity. On the whole, the most probable view seems to be that held by Rutherford himself, but before taking up this one or two additional facts must be mentioned.

If a solution of a uranium salt is precipitated by ammonium carbonate and an excess of the reagent added, most of the precipitate dissolves, but the slight residue is strongly radioactive. The substance is called uranium X. In a somewhat similar manner thorium X was obtained from thorium. The uranium X and the thorium X are highly radioactive and the uranium and thorium, after these constituents

have been separated, are nearly inactive. The uranium X and thorium X, however, soon lose their radioactivity, while the comparatively inactive uranium and thorium *regain* theirs after a time and from them new quantities of radium X and thorium X can be separated. Another matter of interest is that, the *loss of activity by uranium X and thorium X proceeds at the same rate as the gain in activity by the inactive uranium and thorium*. With these facts in mind we can now understand Rutherford's theory of radioactivity. "The atoms of the radio-elements suffer spontaneous disintegration, each disintegrated atom passing through a succession of well-marked changes, accompanied, in most cases, by the emission of α -rays.

"The expulsion of an α -particle, of mass about twice that of the hydrogen atom, leaves behind it a new system, lighter than the original one, and possessing chemical and physical properties quite different from those of the original element. The new system again becomes unstable and expels another α -particle. The process of disintegration, once started, proceeds from stage to stage, one or more α -particles being projected until the last stages are reached, when the β - and γ -rays appear.

"The term *metabolon* has been suggested as a convenient expression for each of these changing atoms, derived from the successive disintegration of the atoms of the radio-elements. Each metabolon, on an average, exists only for a limited time. The various metabolons from the radio elements are distinguished from ordinary matter by their great instability and, consequently, rapid rate of change. Since a body which is radioactive must, *ipso facto*, be undergoing change, it follows that none of the active products, for example, the emanations and thorium X, can consist of any known kind of matter; for there is no evidence to show that inactive matter can be made radioactive, or that two forms of the same element can exist, one radioactive and the other not."

The radioactive elements are, then, undergoing decomposition as described above, giving out the three kinds of rays, emitting heat energy and forming an emanation which is also unstable. This likewise undergoes decomposition, giving radioactive rays, emitting large quantities of heat and yielding, as one of its decomposition-products, the element helium.

HARRY C. JONES.

ANALYTICAL CHEMISTRY. By F. P. TREADWELL, PH.D., Professor of Analytical Chemistry in the Polytechnic Institute of Zurich. Translated with the author's permission from the second German edition by WILLIAM T. HALL, S.B., Instructor in Chemistry, Massachusetts Institute of Technology. Vol. II., Quantitative Analysis. First edition, first thousand. New York: John Wiley & Sons. 1904. 8vo. pp. xii + 654. 96 figures. Price, cloth \$4.00.

The first volume of this work, "Qualitative Analysis," was reviewed in an earlier number.¹

¹ THIS JOURNAL, 30, 244.

When a chemist examines a book on quantitative analysis he must needs compare it with the standard—with the book which we all studied—the great text-book of Fresenius. Many of us have desired a book which should retain the valuable characteristics of “Fresenius” and avoid its prolixity, its confused arrangement, its repetition and its retention of methods of doubtful value. Above all, we have desired a work which should encourage the student to think, instead of blindly following “the directions in the book.” This volume supplies these needs.

Mr. Hall’s translation is excellent ; he has had the advice and assistance of Professors Fay, Moore and Gill and he was permitted to use the notes which Professor Treadwell has collected for his third edition.

As an example of the simplicity of the book, I quote the treatment of magnesium and the alkaline earth metals. For magnesium, determinations as sulphate, oxide and pyrophosphate, with special attention to the method of Gibbs and that of Newbauer.

For calcium, precipitation as oxalate, weighing as oxide ; determination as sulphate, as carbonate. For strontium, determination as sulphate, as oxide. For barium, determination as sulphate, as chromate.

Separations : Ca from Mg and alkalies ; precipitation of Ca as oxalate. Ba from Mg ; precipitation of Ba as sulphate. Sr from Mg ; precipitation of Sr as sulphate. Ba, Sr, Ca, or Sr and Ca from Mg ; precipitation of earths as oxalates and removal of traces of Ba and Sr from filtrate by precipitation as sulphate. Separation of Ba, Sr, Ca ; treatment of nitrates with alcohol-ether, dissolving residue in water and precipitation of Ba as chromate, of Sr as sulphate. Professor Treadwell thinks that all other methods give incorrect results and does not mention them.

As an example of completeness and of improved methods, consider those for determining vanadium ; precipitation of vanadic acid from solution of sodium vanadate ; (a) Rose’s method by mercurous nitrate ; (b) Roscoe’s method by lead acetate. Methods for separation of vanadic from arsenic acid, from phosphoric acid ; of vanadium from molybdenum ; analysis of vanadinite ; determination of vanadium in pig iron ; Hillebrand’s separation of vanadium and chromium in iron ores.

As examples of volumetric methods, determinations of percarbonates, of persulphates, of hydroxylamines by permanganate and many other new and improved processes.

The chapter on gas analysis is excellent. Indeed this is a most admirable book ; it should be examined by all teachers and chemists interested in quantitative analysis. E. R.

DIE BEZIEHUNGEN ZWISCHEN ÄQUIVALENTVOLUMEN UND ATOMGEWICHT. Ein Beitrag zur Festigung und Vervollständigung des periodischen Systems der Elemente. Von DR. W. BORCHERS, Geh. Regierungsrat, Professor der Metallurgie und Vorstand des Instituts für Metallhüttenwesen und Elektrometallurgie an der königl. techn. Hochschule zu Aachen. Halle, a. S. : Verlag von Wilhelm Knapp. 1904. pp. 13. Price, M. .80.

In this little pamphlet the author brings out, in an interesting manner, certain relationships between the atomic weights of the elements and their equivalent volumes. By this term is meant the volume, in cubic centimeters, which is occupied by the weight, in grams, of a substance in the solid form which, when ionized, can carry a charge of 96540 Coulombs. The work of Lothar Meyer and Seubert, who plotted curves showing regularly recurring maxima and minima, is familiar to all chemists. Borchers obtains a similar " wave system of especially remarkable regularity." As might be expected, the curve is, in general, much like that of Meyer and Seubert, although, as Borchers points out, he had to introduce a third factor—valence—in addition to the atomic weight and specific gravity which were taken into account by the earlier workers. In all cases the maximum valence was chosen in making the calculations, though the alteration produced in the curve when the other possible valences of copper, silver and gold were taken into account, are unimportant.

Because his curve is so regular, Borchers thinks that the conclusions drawn from it should be correspondingly reliable. He predicts that new elements will be discovered to occupy vacancies at certain points on his curves. Among others are two new alkali metals, one liquid and the other, perhaps, gaseous.

The pamphlet is an interesting contribution to the literature of the Periodic System. C. E. W.

THE CHEMICAL ENGINEER, Vol. I., No. 1, November, 1904. Allentown, Pa. : The Chemical Engineer Publishing Co. Price, \$3.00 per annum.

The nature of this publication is sufficiently indicated by its title. The number includes articles by Messrs. Shimer and Blair. An index is also provided which, it is stated, will include the title and an indication of the contents of all papers on applied chemistry published in other journals. In view of the scope of the " Journal of the American Chemical Society,"

and of the "Journal of the Society of Chemical Industry," a new publication, covering essentially the same ground, will have to justify its existence by some features of peculiar excellence. Unfortunately, *The Chemical Engineer* entirely fails to do this: the good papers it contains would have found ready acceptance elsewhere and the others ought not to be printed. The proprietor cannot be congratulated on his proof-reader, the report of the New York meeting of the Society of Chemical Industry is a wonderful jumble of inaccuracies and will certainly not conduce towards the object of the journal, which, in the words of its anonymous editor, is to "be useful."

J. B. T.

CHEMISCHE NOVITÄTEN, Jahrgang I., Number 1, Oct. 15, 1904. Leipzig: Gustav Foch. Price, M. 2.50 per annum.

This little monthly publication is devoted to the bibliography of recently published works on pure and applied chemistry and chemical technology. The present number contains an interesting article by Prof. Ostwald, on the "History of Chemical Text-books." Subsequent numbers will include contributions from President Remsen, Geheimrat Ehrlich and Professor Arrhenius.

J. B. T.

AMERICAN CHEMICAL JOURNAL

ON BILIRUBIN, THE RED COLORING-MATTER OF THE BILE.

BY W. R. ORNDORFF AND J. E. TEEPLE.

1. Preparation and Analyses of Bilirubin.

All the bilirubin used in this work was obtained from ox-gallstones furnished by Armour & Co., of Chicago. We desire to express our thanks to this firm for their kindness and our appreciation of the interest they have taken in the investigation, during which we have used over a pound of the stones. Nearly all of them were bilirubin calcium stones, very few were composed of calcium carbonate and none were cholesterin stones. After being removed from the gall-bladder, they were drained, dried at 100° and then sent to us. The method of separation of the bilirubin from the gallstones first adopted was to thoroughly dry the stones at 100° , powder and sift through a 30-mesh sieve, extract with ether in a Soxhlet apparatus until exhausted (12-20 hours), dry again and

exhaust with chloroform in the same way (30-40 hours). The material was then dried once more to remove the chloroform, placed in a large evaporating dish and extracted with successive portions of boiling, distilled water until exhausted. This method of procedure removed fat, lecithin, cholesterin, uncombined bilirubin and other bile pigments soluble in ether or chloroform and bile or other substances soluble in water. The material remaining, which had a deep red color, was then digested for several hours with *excess* of very dilute hydrochloric acid, washed by decantation until the filtrate ceased to give any reaction either for calcium or for chlorides; dried thoroughly and extracted in a Soxhlet apparatus, first with ether (2 hours), then with absolute alcohol, until the alcoholic filtrate had only a faint yellow color, (6 hours) and finally with pure chloroform until exhausted (125 hours). Fresh chloroform was used every 8 hours and all extractions and other work with this solvent and bilirubin were done in a photographic dark-room.

The chloroform extracts, containing the bilirubin, were concentrated by distilling off the excess of chloroform on the water-bath, the bilirubin was precipitated by absolute alcohol and the mixture heated on the water-bath until most of the chloroform had been removed. The alcohol was then decanted and the precipitated bilirubin boiled repeatedly with absolute alcohol until exhausted, in order to remove the so-called biliverdin, biliprasin, bilifuscin and any other soluble material.

The product thus obtained was found not to be *completely* soluble in chloroform,¹ though it left no ash when burned and the amount which did not go into solution was very small. It was therefore boiled with large quantities of chloroform, in successive portions, the solution filtered twice, to remove suspended matter, concentrated, precipitated with absolute alcohol,

¹ In nearly all prolonged extractions with the Soxhlet apparatus we found that the extracted material was not entirely soluble in the solvent used. This is probably due to some of the substance being carried over mechanically.

washed with alcohol, filtered, dried and if not completely soluble in chloroform, the process was repeated.

With one lot of gallstones the following results were obtained: 130 grams of the stones, dried at 100° , gave 8 grams of ether extract, 5.2 grams of chloroform extract, 9.5 grams of water extract, 20 grams of hydrochloric acid extract, 1.1 grams of ether extract, 2 grams of alcoholic extract and 22.5 grams of the crude bilirubin. The residue (about 60 grams) consisted of the so-called bilihumin.

Some of the product, completely soluble in chloroform, was then recrystallized twice from dimethylaniline (b. p. $192^{\circ}.2-192^{\circ}.8$). This specimen crystallized in beautiful reddish-yellow, minute needles and, under the microscope, appeared perfectly homogeneous and free from amorphous matter. A mixture of 2 parts chloroform and 1 part dimethylaniline gave even better crystals (see Fig. III.). Chloroform solution of quinine was also found to dissolve large quantities of the bilirubin, which separated in crystals nearly as good as the preceding ones.

Analyses:

1. Bilirubin crystallized *twice* from dimethylaniline, completely soluble in chloroform and leaving no ash, dried at 120° .

0.269 gram bilirubin gave 17.7 cc. N/10 NH_3 or 0.02485 gram N. Kjeldahl-Gunning method, modified to include nitrogen of nitrates, as adopted by the Association of Official Agricultural Chemists, 1898.¹

2. Same product and method as No. 1. Digested three-quarters of an hour longer than No. 1.²

0.3444 gram bilirubin gave 22.7 cc. N/10 NH_3 or 0.03187 gram N.

3. Product like No. 1, but a different preparation. First reduced the bilirubin with zinc and sulphuric acid and then

¹ Bulletin 46 (revised) U. S. Department of Agriculture, Division of Chemistry, p. 17.

² Analyses 1 and 2 were made by Professor G. W. Cavanaugh, Chemist of the Agricultural Experiment Station at Cornell University, to whom we wish to express our thanks.

used the Kjeldahl-Gunning method, adopted also by the Association of Official Agricultural Chemists. Product dried at 125° .

0.2977 gram bilirubin gave 19.07 cc. N/10 NH_3 or 0.02679 gram N.

4. Product like No. 1, but a different preparation. First reduced the bilirubin by the action of P_2I_4 and H_2O (Chenel¹), then used the Kjeldahl-Gunning method. Product dried at 125° .

0.2158 gram bilirubin gave 14.12 cc. N/10 NH_3 or 0.01982 gram N.

5. Product like the preceding ones but a different preparation (Dumas method). Carbon dioxide generated in a Kipp apparatus from marble that had been thoroughly boiled in water to expel air. Carbon dioxide ran three to four hours to expel all air. Product dried at 130° .

0.2208 gram bilirubin gave 19.2 cc. N, 732 mm. (cor.) and $24^{\circ}.5$.

6. Same product and method as No. 5.

0.1728 gram bilirubin gave 15.25 cc. N, 729.8 mm. (cor.) and 26° .

7. Mixture of what remained of products 3 to 6 (Dumas method). Carbon dioxide generated from boiled, supersaturated sodium bicarbonate solution and boiled, dilute sulphuric acid.

0.1659 gram bilirubin gave 14.2 cc. N, 733.95 mm. (cor.) and $25^{\circ}.8$.

8. Product recrystallized from dimethylaniline, not completely soluble in chloroform but leaving a negligible residue, dried at 130° . Dumas method, using magnesite and heating it in a separate combustion tube, on a short furnace. The copper oxide and the copper spiral were heated for some time in a current of carbon dioxide and allowed to cool in this gas, in order to get rid of occluded air, hydrogen, or carbon monoxide.²

¹ Bull. Soc. Chim., 1892, (1), p. 321.

² Following a suggestion of Prof. H. N. Morse of the Johns Hopkins University.

0.1659 gram bilirubin gave 14.2 cc. N, 748.8 mm. (cor.) and 27° .¹

9. Product precipitated from chloroform by alcohol, completely soluble in chloroform, dried at 130° . Same method as No. 8.

0.2084 gram bilirubin gave 17.45 cc. N, 742 mm. (cor.) and 24° .

10. Same product as No. 9, method as given in Gattermann. Employed a copper spiral, which was reduced in methyl alcohol and then heated in a current of carbon dioxide before use, to expel occluded hydrogen or carbon monoxide.

0.2050 gram bilirubin gave 0.5048 gram CO_2 and 0.1133 gram H_2O .

11. Same product as No. 8. Same method as No. 10.

0.2336 gram bilirubin gave 0.5761 gram CO_2 and 0.1248 gram H_2O .

12. Same product as Nos. 9 and 10. Method of Benedict,² using a weighed amount of rock candy to furnish the reduced copper. Dried at 140° .

0.2594 gram bilirubin and 0.1270 gram sugar gave 0.8300 gram CO_2 and 0.2078 gram H_2O . CO_2 from the sugar; calculated 0.1960 gram; H_2O from the sugar; calculated 0.07355 gram, leaving 0.6340 gram CO_2 and 0.13425 gram H_2O from the bilirubin.

13. Same product and method as No. 12.

0.3025 gram bilirubin and 0.1348 gram sugar gave 0.9504 gram CO_2 and 0.23995 gram H_2O . CO_2 from the sugar, calculated 0.2080 gram; H_2O from the sugar; calculated 0.07805 gram, leaving 0.7424 gram CO_2 and 0.1619 gram H_2O from the bilirubin.

14. Same product as Nos. 9, 10, 12 and 13. Analysis made by Prof. Benedict, using his own method.

0.1504 gram bilirubin and 0.1126 gram sugar gave 0.5411 gram CO_2 and 0.1543 gram H_2O . CO_2 from the sugar; calculated 0.1737 gram; H_2O from the sugar; calculated 0.0652

¹ Analysis No. 7 was made Feb. 23, 1901; analysis No. 8 April 27, 1901.

² THIS JOURNAL, 23, 343. According to Benedict, the reduced copper spiral, as ordinarily used, might contain enough carbon dioxide or other carbon compound to vitiate the results.

gram, leaving 0.3674 gram CO_2 and 0.0891 gram H_2O from the bilirubin.

15. Same product and method as No. 14. Analysis made by Prof. Benedict.

0.1512 gram bilirubin and 0.1017 gram sugar gave 0.5253 gram CO_2 and 0.1409 gram H_2O ; CO_2 from the sugar; calculated 0.1569 gram; H_2O from the sugar; calculated 0.0589 gram, leaving 0.3684 gram CO_2 and 0.0820 gram H_2O from the bilirubin.

16. Same product as No. 14 and 15. Determination made by method used in cases in which the nitrogen is in the un-oxidized condition.¹

0.1245 gram bilirubin gave 0.2990 gram² CO_2 and 0.0675 gram H_2O .

The sugar used in experiments 14 and 15 gave the following results :

0.2026 gram gave 0.3123 gram CO_2 and 0.1181 gram H_2O .

	Calculated.	Found.
C	42.07	42.04
H	6.49	6.50

Summary of Results.³

No.	Nitrogen.	No.	Carbon.	Hydrogen.
1	9.24	10	67.15	6.18
2	9.25	11	67.25	5.99
3	9.10	12	66.66	5.80
4	9.19	13	66.93	5.99
5	9.36	14	66.62	6.63(?)
6	9.39	15	66.45	6.07
7	9.17	16	65.50(?)	6.07
8	9.31			
9	9.16			
		Nitrogen.	Carbon.	Hydrogen.
Averages ⁴		9.24	66.84	6.02
Calculated for $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_3$		9.81	67.08	6.34
" " $\text{C}_{34}\text{H}_{36}\text{N}_4\text{O}_7$		9.17	66.61	5.94

¹ THIS JOURNAL, 23, 337.

² Tube broke before completion of the analysis.

³ The international atomic weights ($\text{O} = 16$) have been used throughout this paper.

⁴ The percentages of carbon in No. 16 and hydrogen in No. 14 are omitted in this average.

The above analyses were made on seven different preparations, by three men, using seven variations of methods for determining the nitrogen and three modifications for the carbon and hydrogen. The more refined and accurate the method of analysis used, the greater seemed to be the divergence from the percentages required for the formula $C_{16}H_{18}N_2O_3$. In the earlier stages of this work we thought that the bilirubin might be impure. To obtain a pure product we therefore used every precaution that had ever been suggested, besides some additional ones. Most of the determinations were made with crystallized products, which appeared perfectly homogeneous when examined under the microscope. No amorphous matter could be detected in the mass of crystals and only one kind of crystals was present. These all had the same extinction angle. The bilirubin, precipitated from chloroform by alcohol, the product which Städeler and Maly analyzed, gave us practically the same results as the crystallized products such as Küster and von Zumbusch analyzed. Analysis No. 1 was made on the first crystals and No. 5 on the last ones from the same dimethylaniline with successive portions of bilirubin dissolved in it. There was, therefore, no evidence of a fractional separation from this solvent. We sometimes noticed when dissolving, in chloroform, a product precipitated from chloroform by alcohol, that one portion of the material seemed to dissolve more readily than another, but we attributed this to differences in the mechanical state of division. So far as we could determine, the finer particles of the bilirubin went into solution in the chloroform first, leaving the coarser material undissolved.

From the descriptions of bilirubin given in the literature, our products compared very favorably, in purity, with the best that any previous investigators had obtained and the analyses certainly indicated this.

Difficulties in analyzing such substances are frequently encountered, for example, von Zumbusch¹ states that he could get no ammonia at all from bilifuscin by any of the Kjeldahl

¹ Z. physiol. Chem., 31, 454.

methods, although the compound gave over 8 per cent of nitrogen by the absolute method. This appears all the more astonishing in view of the fact that he found he could determine the amount of nitrogen in bilirubin by the Kjeldahl method. Nencki and Zaleski¹ found that haemin and haematoporphyrin require heating for hours at a white heat to give off all the nitrogen and, when analyzed by the Kjeldahl method, the digestion must be continued for some hours after the fluid is decolorized. We expected to find such difficulties here and after the first two analyses, by the Kjeldahl method, had failed to give the amount of nitrogen required by the formula $C_{16}H_{18}N_2O_3$, we tried all the methods mentioned above. Bilirubin is very resistant to the usual analytical treatment. Prolonged heating at a high temperature, using a Jena glass combustion tube, is essential to obtain all the nitrogen by the Dumas method and vigorous reduction and lengthy digestion with sulphuric acid and potassium sulphate, after the fluid has been decolorized, are necessary in determining the nitrogen by the Kjeldahl method. Notwithstanding all these precautions, however, none of the determinations had given as much as 9.4 per cent of nitrogen (while the theory demanded 9.81 per cent) and we were satisfied that there was no more than this in the substance. Likewise, in the carbon and hydrogen determinations, we regarded those made by Benedict's method as most accurate because there were fewer sources of error. The average of these results, including those made by Professor Benedict and our own, was C 66.66 and H 5.98 per cent; the theory for $C_{16}H_{18}N_2O_3$ required 67.08 and 6.34 per cent, respectively.

As, therefore, we had no reason to suspect the analytical results and as our product seemed homogeneous and as pure as those of previous investigators, we examined all the analyses of bilirubin which had been published and upon which was based the commonly accepted formula, $C_{16}H_{18}N_2O_3$, first ascribed to it by Städeler, in 1864. The following are the results of all the analyses published between that time and 1902 :

¹ Z. physiol. Chem., 30, 387.

On Bilirubin.

Investigator.	C.	H.	N.	Remarks.
Städeler (1864)	67.15 67.11	6.27 6.12	9.59	N. by the soda-lime method. Bilirubin precipitated from chloro- form by alcohol.
Thudichum (1868)	66.02 66.41 65.61	5.97 6.13 5.95	9.05 9.49 8.82 }	N. by the absolute method. N. by the soda-lime method. Bilirubin precipitated from chloro- form by alcohol.
Maly (1868)	67.16	6.18		Bilirubin precipitated from chloro- form by alcohol.
" (1874)	67.52 66.95	6.22 6.29		
Küster (1898)	I. { 66.94 66.99	7.03 6.88	11.48 11.35	N. by the absolute method. Bilirubin crystallized from dimethyl- aniline.
	II. 67.45	6.77	10.21	Only the last of the three prod- ucts was both free from ash and completely soluble in chloroform.
Von Zumbusch (1900)	III. 67.19	6.46	10.12 9.30	Bilirubin crystallized from dimethyl- aniline. N. by the Kjeldahl method.
Average of all analyses on prod- ucts soluble in chloroform and free from ash				
Average found by us				
Theory for $C_{16}H_{18}N_2O_3$				
Theory for $C_{34}H_{36}N_4O_7$				
	66.79 66.84 67.08 66.61	6.19 6.02 6.34 5.94	9.39 9.24 9.81 9.17	

In Hoppe-Seyler's "Handbuch der physiol. und pathol. chemischen Analyse," H. Thierfelder, seventh edition, p. 287, the following statement occurs: "Die Zusammensetzung und die Eigenschaften des Bilirubins sind von Städeler festgestellt worden. Maly hat diese Angaben bestätigt und die Analysen von Hoppe-Seyler lassen gleichfalls keinen Zweifel an der Richtigkeit der Städelerschen Formel." We have been unable to find any record of these analyses of Hoppe-Seyler.

The greatest difference between our results and the theoretical values for the formula $C_{16}H_{18}N_2O_3$, occurs in the nitrogen, where it amounts to 6 per cent of the total. Examining the previous nitrogen determinations, we find that Städeler based his formula on but one and that by the, now obsolete, "soda-lime" method. Thudichum's results vary too widely to carry much weight and only one of his nitrogen determinations was made by the absolute method, their average, however, is still lower than ours. Maly did not determine the nitrogen in the bilirubin he analyzed. Küster's four values for nitrogen are all much higher than the theory requires (from 3 to 17 per cent of the total) and only the last of his three products was *both* completely soluble in chloroform and free from ash. Von Zumbusch's analysis, by the Kjeldahl method, agrees with ours. A comparison of the averages of all analyses, on products completely soluble in chloroform and free from ash, with the averages found by us, shows them to be practically identical.

We were, therefore, convinced that bilirubin, the pigment occurring in ox-gallstones, soluble in chloroform, alkalies and dimethylaniline, practically insoluble in alcohol, ether and petroleum ether, prepared by any of the methods heretofore used, did not have the composition represented by the formula $C_{16}H_{18}N_2O_3$. These results were published in July, 1901, in a preliminary paper,¹ with the provisional statement that they agreed better with the formula $C_{34}H_{36}N_4O_7$, than with any other.

In consequence of the publication of our work Küster² was led to re-examine the pigment (April, 1902). Working with

¹ THIS JOURNAL, 26, 86.

² Ber. d. chem. Ges., 35, 1268.

a large quantity of material, 1000 grams of the dried ox-gallstones and 200 grams of biliary concrement obtained from a horse, he was able to demonstrate that what has, hitherto, been called bilirubin is a mixture of *at least two* substances, differing only in their degree of solubility in chloroform and in their percentage composition. He also states in a foot-note, "Die Resultate von Orndorff und Teeple (Amer. Chem. Jour., **26**, 87) erklären sich vielleicht durch einen Gehalt ihres Bilirubins an leichter löslichen Farbstoff."

For the product least soluble in chloroform he retains the name bilirubin and his analyses of this compound, recrystallized from dimethylaniline, give results which now agree remarkably well with those demanded by the formula $C_{16}H_{18}N_2O_3$, though he unfortunately omits all analytical data. The more soluble compound he was not able to obtain pure, but he found, in a general way, from the products which he analyzed, that it contained less nitrogen and usually less carbon, than the substance for which he retains the name bilirubin.

As stated above, we had repeatedly observed these differences in the solubility of the various products in chloroform, but had attributed them to differences in the mechanical state of division of the products, supposing that the finer material dissolved and left the coarser. We now repeated the work and were able to confirm Küster's statement regarding the presence of two substances in the chloroform extract which differed only in the degree of their solubility in this solvent. Our method of obtaining the bilirubin from the gallstones was the same as Küster's, except that we subjected the material to an exhaustive extraction with alcohol before treatment with chloroform and that we did not deem it wise, in extracting, to use such small amounts of chloroform that the bilirubin separated in crusts, nor did it seem best to crystallize the material from a solvent with a boiling-point so high as that of dimethylaniline. We therefore exhausted the material with large amounts of chloroform, filtered, distilled off a part of the solvent on the water-bath and allowed the liquid to cool slowly. The crystalline product, which separates after standing for a day or two, was filtered, boiled with alcohol and re-

peatedly recrystallized, in the same manner, from large amounts of chloroform. This method gives a perfectly pure crystalline product, entirely free from the material more soluble in chloroform. It has, of course, the disadvantage that large quantities of chloroform are required. The product, however, is much superior to that obtained in any other way. The analyses were made with bilirubin obtained in this way and dried to constant weight at 123° :

1. 0.1438 gram substance gave 12.5 cc. N at $20^{\circ}.5$ and 753.8 mm. (cor.) Absolute method. Carbon dioxide from magnesite.

2. 0.1557 gram substance gave 13.3 cc. N at $19^{\circ}.8$ and 749.5 mm. (cor.) Absolute method. Carbon dioxide from magnesite.

3. 0.1592 gram substance gave 10.9 cc. of N/10 ammonia. Kjeldahl-Gunning method after first reducing with zinc dust and sulphuric acid.¹

4. 0.1607 gram substance gave 11.18 cc. of N/10 ammonia. Kjeldahl-Gunning method after first reducing with P_2I_4 and water.

Summary.

No.	Nitrogen.
1	9.83
2	9.65
3	9.60
4	9.77
Calculated for $C_{16}H_{18}N_2O_3$	9.81

These results, together with those recently published by Küster, show, beyond all doubt, that the formula of the compound less soluble in chloroform is $C_{16}H_{18}N_2O_3$ and that all analyses recorded up to 1902 were made on a mixture of this less soluble bilirubin, with a small amount of another substance closely resembling it in all respects, except that it contained a lower percentage of nitrogen and was more soluble in chloroform.

Whether the pure bilirubin thus isolated occurs in fresh bile is unknown.²

¹ This analysis was made for us by Professor G. W. Cavanaugh of the Agricultural Experiment Station at Cornell University.

² *Vide* Thudichum: *Virchow's Arch.*, 156, 384 (1900).

2. Properties of Bilirubin.

a. Crystallization and Crystal Form.—Amorphous bilirubin, precipitated from chloroform by alcohol, is red, when crystallized from dimethylaniline or chloroform the color is deep red; the thinner crystals, observed under the microscope, are yellowish-red by transmitted light.

Bilirubin has weak acidic properties, somewhat like those of the phenols; it dissolves readily in dilute solutions of the alkalis and alkaline carbonates, more slowly in concentrated solutions, particularly of the alkaline carbonates. Carbon dioxide precipitates it, almost completely, in the amorphous form, from solution in dilute alkalis. The chloroform solution of the pigment is completely decolorized by shaking with dilute alkali solution. Solution of bilirubin in ammonia does not reduce ammoniacal silver nitrate even when boiled, indicating that the substance does not contain an aldehyde group.

Bilirubin may be crystallized from dimethylaniline, from a mixture of dimethylaniline and chloroform, or, best, from chloroform alone. The crystals from dimethylaniline are usually cigar shaped¹ and incompletely formed, those from a mixture of dimethylaniline and chloroform are more perfect (see Fig. III.). If the bilirubin has been carefully purified from the more soluble product, the best crystals may be obtained from chloroform (see Figs. I., II. and IV.).² The older statement that bilirubin crystallizes best from impure solutions is certainly wrong. When perfectly pure, a drop of a chloroform solution of bilirubin, allowed to evaporate spontaneously, deposits nothing but crystallized material. Two specimens, crystallized from chloroform, were submitted to Prof. A. C. Gill, of the Mineralogical Department of Cornell University, who reports as follows: "The crystals are columnar in shape, with the end faces almost at right angles to the direction of elongation. They are monoclinic or triclinic, probably the former, as judged from the very indefinite optical figure in converged polarized light. They have an extinction

¹ *Vide* Küster: Z. physiol. Chem., 26, 325 for an illustration of these crystals.

² We desire to express our thanks to Prof. S. H. Gage, of Cornell University, for these four photographs.

angle of 9° – 10° , show high double refraction and slight pleochroism. The color of the thinnest crystals is orange-yellow, that of the thickest brick-red. The material seemed to be entirely crystalline, as no amorphous matter was observed. All the crystals have the same extinction angle, which also indicates that they are probably monoclinic, the columnar shape being due to the development of the prism." When a drop of a saturated solution of *pure* bilirubin, in chloroform, is allowed to evaporate on a microscope slide, part of the crystals formed are rectangular tablets, like those described above, the remainder consists of long elliptical needles, the whole field (plates and needles), however, has the same extinction angle.

With regard to the crystals from a mixture of dimethylaniline and chloroform, Dr. Gill reports as follows: "The crystals form stout needles or elongated columns, having an orange-yellow color and showing a distinct, but not strong, pleochroism. The ends are, in some cases, sharply terminated by faces, inclined about 60° to the direction of elongation. Most of these crystals do not extinguish between crossed Nicols, thus indicating a strong dispersion or, more likely, a twin structure, which is not apparent from their external form. Some of those with broken ends show strong double refraction and sharp extinction, at an angle varying from $2^{\circ}.5$ to 12° . The crystals are either monoclinic or triclinic, as shown by this extinction angle."

b. Solubility.—Thudichum gives the solubility of bilirubin as 1 in 586 parts of chloroform, while Küster found it to be 1 : 567. Neither investigator describes his method of determining the solubility or, indeed, gives any details. Pure, crystallized bilirubin dissolves very slowly in chloroform, even when boiled for some time. In order to prepare a saturated solution we found it was best to boil the bilirubin with chloroform (using an upright condenser) for 8–12 hours, filter, distil off a portion of the solvent on the water-bath and let the liquid stand till next day. Crystals of bilirubin slowly separate and rise to the surface. If the amount of bili-

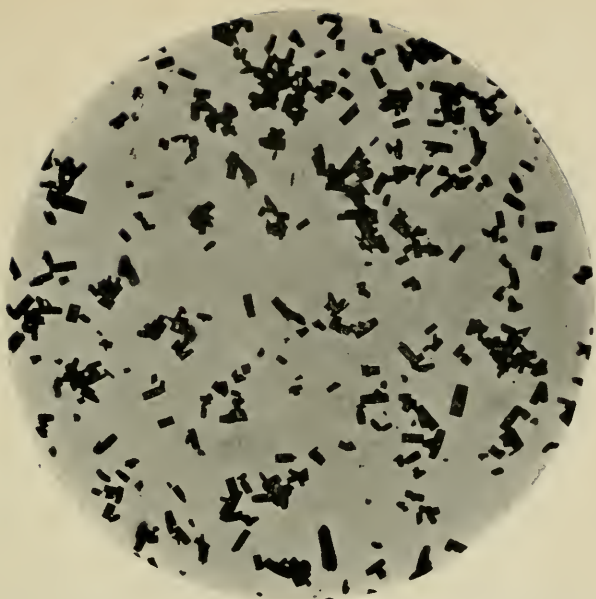


Fig. I.—Bilirubin crystallized from chloroform. Magnified 390 times.

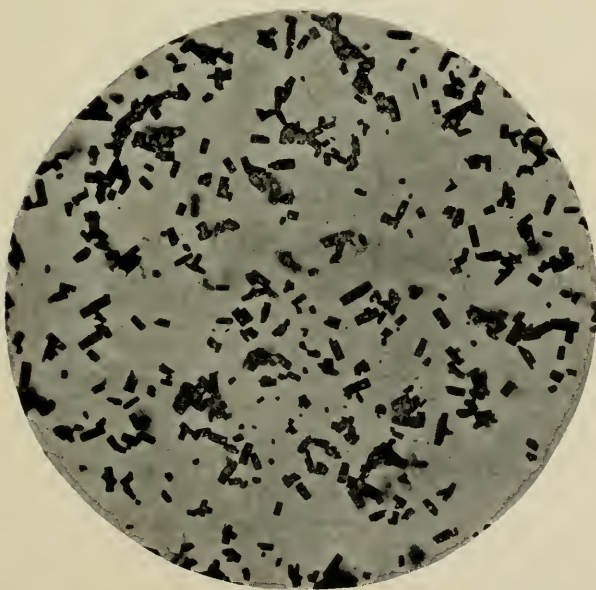


Fig. II.—Bilirubin crystallized from chloroform. Magnified 390 times.

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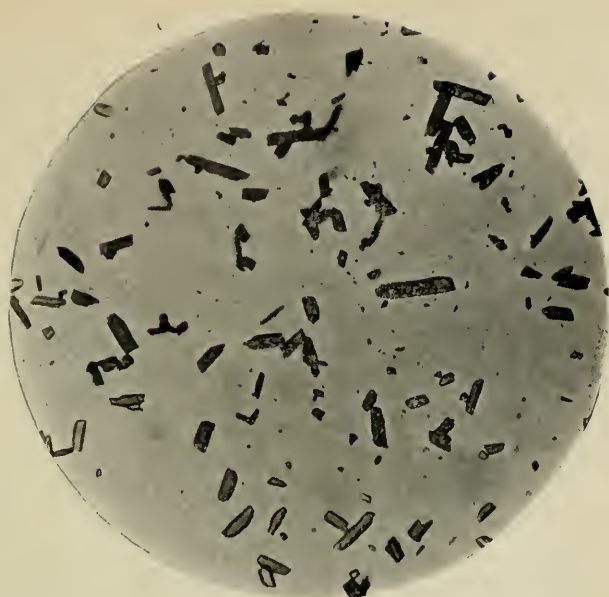


Fig. III —Bilirubin crystallized from a mixture of dimethylaniline and chloroform. Magnified 330 times.

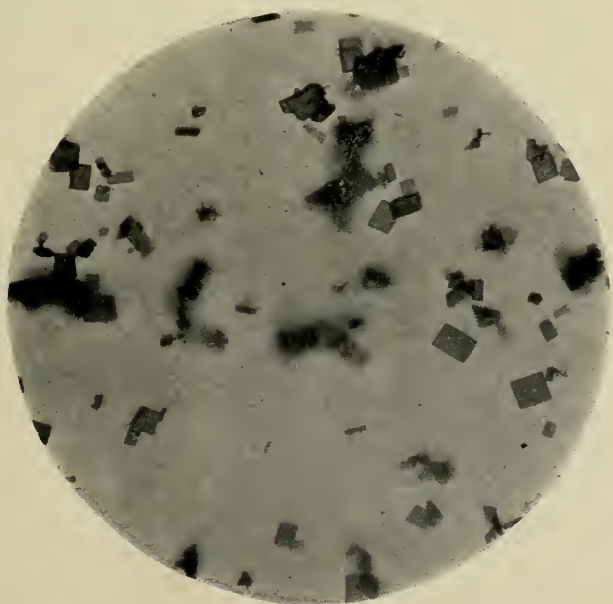


Fig. IV.—Bilirubin crystallized from chloroform by cooling very slowly. Magnified 330 times.

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rubin present in this solution be determined by removing the crystals and evaporating a weighed quantity of the filtrate to dryness on the water-bath, the solubility will be found to be very nearly the same as given by Thudichum and Küster, provided the solution has only stood in contact with the crystals a few hours. This does not, however, represent the true solubility of bilirubin in chloroform, for, when the liquid is allowed to stand longer in contact with the crystals, more are deposited, showing that the solution is still supersaturated. The condition of equilibrium is not reached for several days at least. The following results were obtained by the method described above. After the mixture had stood the required length of time, a small portion of the solution was filtered from the crystals, weighed, evaporated to dryness on the water-bath and the residual bilirubin also weighed. The remainder of the solution was allowed to stand in contact with the crystals for several days longer, when another portion was treated in the same manner. The solubility was determined at 23° :

Experi- ment.	Time the solu- tion stood with crystals. Days.	Weight of the solution in grams.	Weight of bilirubin in grams.	Solubility, 1 part in
1	1	32.42	0.0479	676
	6	23.259	0.0263	884
2	5	26.83	0.0303	884
	12	20.902	0.0208	1004
3	10	39.886	0.0409	974

We attempted to get a saturated solution of bilirubin in chloroform by boiling 0.3 gram of pure, crystallized material, for 4 hours, with 45 grams of chloroform, in a reflux apparatus. After filtering the cold solution we found that 29.534 grams of it gave 0.0296 gram bilirubin, corresponding to 1 part in 997 parts of chloroform.

In order to avoid the formation of supersaturated solutions we endeavored to determine the solubility of the bilirubin in chloroform by shaking the two in sealed tubes. The following results were obtained by Mr. F. C. Robinson, to whom we wish to express our thanks :

Time of contact.	Weight of solution in grams.	Weight of bilirubin in grams.	Solubility, 1 part in
10 days shaking and 3 days standing	11.12	0.00286	3887
10 days shaking and 34 days standing	2.97	0.00115	2582
Temperature, 20°.1.			

From these results it will be seen that the tendency of bilirubin to form supersaturated solutions, in chloroform, is very great and that the determination of its solubility in this medium is a matter of considerable difficulty.

Chloroform solution of anhydrous quinine dissolves much larger quantities of bilirubin than chloroform alone, and when the solution evaporates spontaneously, fairly good crystals are deposited, some being well formed, others imperfect, like those from dimethylaniline. The bilirubin may also be precipitated from the chloroform-quinine solution by absolute alcohol.

We endeavored to determine the molecular weight of pure bilirubin in the chloroform-quinine solution by the ebullioscopic method, but without success, as the addition of bilirubin caused no perceptible rise in the boiling-point of the solution, probably because the bilirubin combined with the quinine and so did not increase the number of molecules present.

When bilirubin is fused with potassium hydroxide it gradually dissolves, forming, finally, a colorless liquid and evolving small amounts of ammonia and of a pyrrol derivative, as was shown by the fact that the vapors slowly turned red litmus paper blue and reddened a pine splinter, which had been moistened with hydrochloric acid.

3. Attempts to Determine the Presence of Alkyloxy and Alkylimide Groups in Bilirubin.

Bilirubin does not contain an alkyloxy group, as was shown by the fact that, when treated with *pure* hydriodic acid, according to the Zeisel method¹ for determining alkyloxy groups, the amount of silver iodide formed was practically unweighable.

¹ Monats. Chem., 6, 989.

Attempts to determine whether it contains an alkylimide group, by Herzig and Meyer's¹ method, by heating with hydriodic acid and ammonium iodide, did not result so decisively. The sources of error in the method itself are so considerable that the authors acknowledge it to be unreliable where the molecular weight of the substance, in which the alkylimide group is to be determined, is larger than 600. We show, later, that the molecular weight of bilirubin is 572. The following are the results which we obtained :

No.	Weight of bilirubin.	Weight silver iodide.	Per cent CH ₃ .	Theory for one CH ₃ group in C ₃₂ H ₃₆ N ₄ O ₆ .
1	0.3125	0.1200	2.46	2.62
2	0.2845	0.1018	2.29	
3	0.2912	0.0966	2.12	
4	0.2338	0.0515	1.41	
5	0.1921	0.0267	0.89	

Products 1 and 2 were crystallized from dimethylaniline ; they were prepared in the same way as products 1, 2 and 3, the results of the analysis of which are given on p. 217. Apparently they are not entirely free from the substance more soluble than bilirubin, containing a smaller amount of nitrogen ; they may have contained a little dimethylaniline, though they were dried at 120° before being analyzed. Product No. 3 was precipitated from chloroform solution by alcohol and was the same as products 9 and 10, the results of the analysis of which are given on p. 219. It was dried at 130° before analysis. Products 4 and 5 were pure bilirubin, carefully crystallized from chloroform and dried at 123° ; they were the same products as those, 1, 2, 3 and 4, analyses of which are given on p. 219. The *purest* products give the *smallest* percentages for the methyl group and all the results are below the value required for one methyl group to the molecule C₃₂H₃₆N₄O₆. It is highly probable, therefore, that *pure* bilirubin does not contain a methylimide group, though the method seems hardly accurate enough to decide this point absolutely, in the case of a compound with such a large molecular weight.

¹ Monats. Chem., 15, 613.

4. Reduction of Bilirubin.

a. With Zinc Dust.—Bilirubin (1.2 grams) was thoroughly mixed with zinc dust (25 grams), by grinding in a mortar and the mixture carefully heated in a current of hydrogen, in a hard-glass combustion tube, to which was attached a Peligot tube surrounded by ice-water. Greenish-yellow vapors were evolved, which partially condensed to a yellow liquid in the Peligot tube. They had an alkaline reaction and reddened a pine splinter moistened with hydrochloric acid.

When passed through solution of mercuric chloride they gave a precipitate which had all the characteristics of haemopyrrol-mercuric chloride; it dissolved completely in alcohol containing hydrochloric acid and this solution rapidly became colored and showed the urobilin spectrum.

Part of the yellow liquid dissolved in water and gave a white precipitate with Nessler's reagent. On standing, this yellow liquid changed to a dark-brown resinous mass and the Peligot tube acquired a very marked odor of an old pipe. All these properties indicate that the yellow liquid contained haemopyrrol, which was also obtained, later, by the reduction of bilirubin with nascent hydriodic acid.

b. With Sodium Amalgam.—Considerable quantities of bilirubin (over 4 grams) and various bilirubin residues were repeatedly reduced with sodium amalgam, according to Städeler and Maly's¹ directions. The product resulting agreed, generally, in properties with Maly's so-called hydrobilirubin; it gave the same absorption band, the characteristic reaction with zinc chloride and the specific reaction with iodic acid described by Capranica.² It did not seem to us, however, to be a uniform substance and exhibited somewhat different properties when slight changes were made in the method of preparation. We found it impossible to purify the material by recrystallization from any solvent and consequently no further work was done with it. Incidentally, it was noticed that the addition of bromine water to an aqueous alcoholic solution of the "hydro-

¹ Ann. Chem. (Liebig), 161, 368; 163, 77.

² Jahres. Tierchemie, 12, 302.

bilirubin'' decolorized the solution and gave a very voluminous yellow precipitate.

c. With Nascent Hydriodic Acid.—Nencki and Zaleski¹ obtained haemopyrrol, $C_8H_{13}N$, by reducing acethaemin, and Nencki and Marchlewski² made the same product from phyllocyanin, a derivative of chlorophyll, thus establishing a very close relationship between the blood and plant coloring-matters. Later, Küster³ found that Mörner's β -haeminal so gave haemopyrrol, when reduced by Nencki's method. In all these cases the substances were reduced by heating, in glacial acetic acid solution, with hydriodic acid (sp. gr. 1.96) and phosphonium iodide.

As bilirubin is, in all probability, derived from the haemoglobin of the blood, we naturally expected to obtain haemopyrrol from it by reduction. Our experiments on the reduction of bilirubin with zinc dust had shown, indeed, that haemopyrrol could also be obtained from bilirubin, but this method only gave a small yield and the product was hardly pure enough for analysis.

In determining the nitrogen in bilirubin, by the Kjeldahl-Gunning method, we found that a previous reduction with phosphorus tetraiodide and water (the Chenel method) was essential in order, subsequently, to obtain complete oxidation by the sulphuric acid, within any reasonable length of time. Supposing that the bilirubin was here, also, reduced to haemopyrrol, we made a number of experiments with acethaemin to perfect the method and compare the results with Nencki's.

The best procedure was the following: Phosphorus (2 grams) was dissolved in carbon disulphide (about 20 cc.) in a long-necked Kjeldahl flask⁴ and iodine (16 grams) was added slowly, in small portions, shaking thoroughly after each addition until solution is complete. When all the iodine has

¹ Ber. d. chem. Ges., 34, 1003.

² *Ibid.*, 34, 1689.

³ *Ibid.*, 35, 2953.

⁴ Chenel recommends the use of the phosphorus and iodine in the ratio of 1:6, but we obtained better results when we used 1:8, nearly those theoretically required for the compound P_2I_4 . If Chenel's directions are followed, a separation of amorphous phosphorus often occurs when the compound is decomposed with water.

been added and is combined with the phosphorus, the carbon disulphide is distilled at as low a temperature as possible and the last traces of it removed from the crystals of phosphorus tetraiodide by a current of *dry* air. Add the acethaemin (0.2–0.5 gram) and mix thoroughly by shaking with the phosphorus tetraiodide which is then decomposed by hot water (8–10 cc.). The flask is heated on the water-bath for 2–3 minutes, thoroughly shaken, and the liquid prevented from foaming over, by cooling, if necessary. Hydriodic acid and phosphonium iodide are formed and rapidly reduce the substance, which goes completely into solution, yielding, finally, a light yellow liquid. After cooling, the solution is diluted with a little water, partly neutralized with sodium carbonate and enough sodium acetate solution added to combine with the remaining acids, leaving only a small amount of acetic acid free. The mixture is then distilled in a current of carbon dioxide, the distillate being collected in solution of mercuric chloride. The precipitate of mercury haemopyrrol mercuric chloride, $(C_8H_{12}N)_4Hg.(HgCl_2)_4$, is filtered, washed with water, dried over sulphuric acid and weighed.

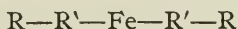
Analysis by Nencki and Zaleski's¹ method :

0.2742 gram mercury compound gave 0.2089 gram HgS.

Percentage of mercury found	65.66
Computed for $(C_8H_{12}N)_4Hg.(HgCl_2)_4$	65.45

This indicates that the product formed by this method of reduction, is identical with the haemopyrrol obtained by Nencki and his co-workers from acethaemin and phyllocyanin and by Küster from β -haemin. This was also indicated by the fact that solutions of the compound turn red on standing and then show the very distinct and characteristic absorption band, the "urobilin" spectrum, exactly as solutions of haemopyrrol do.

If we assume, with Küster,² that the molecule of haematin consists of two parts, as shown in the scheme



¹ Ber. d. chem. Ges., **34**, 1003.

² Ann. Chem. (Liebig), **315**, 184 (1900).

and that only the radicals R are converted into haemopyrrol by reduction, or into the haematinic acids by oxidation, as haemopyrrol and the haematinic acids come from the same part of the molecule,¹ then 1 molecule of acethaemin should yield, on reduction, 2 molecules of haemopyrrol, or 1 molecule of the mercuric chloride double salt, $(C_8H_{12}N)_2Hg.(HgCl_2)_4$, that is, 1 gram of acethaemin should yield 2.345 grams of the mercuric derivative, or 0.3773 gram of haemopyrrol. The best yield we obtained was as follows: 0.54 gram acethaemin gave 0.53 gram of the mercuric chloride double salt, which is equivalent to 42 per cent of the theoretical amount.

Küster² states that he obtained 2 grams of the mercury compound from 5 grams of the β -haemin, equivalent to 0.7 gram of haemopyrrol. One of these figures is evidently a misprint, for the 2 grams of mercury compound correspond to 17.45 per cent of the amount required by theory, while the 0.7 gram of haemopyrrol is equivalent to 37.9 per cent of the theoretical. Nencki and Zaleski³ once obtained 32 per cent of the calculated amount, on the assumption that each molecule of acethaemin yields 4 molecules of haemopyrrol. They do not give the weight of the mercury compound obtained, however and so it is impossible to recalculate their results.

The reason why a larger yield of haemopyrrol is not obtained, is undoubtedly due to the fact that it polymerizes or oxidizes so readily. If we attempt to distil the haemopyrrol with steam, instead of using carbon dioxide, the liquid rapidly darkens, a resinous mass precipitates, and the yield is much diminished. The liquid from which the haemopyrrol has been distilled then shows a very pronounced "urobilin" absorption band. This same change takes place very rapidly when the haemopyrrol solution is allowed to stand, so that it is advisable to distil off the haemopyrrol as soon as the reduction of the acethaemin is completed. This polymerization or resinifying of the haemopyrrol takes place, to some extent, whatever precautions are taken to prevent it, as the liquid left in the distillation-flask always shows the

¹ Ber. d. chem. Ges., **35**, 2953 (1902).

² *Ibid.*, **35**, 2953 (1902).

³ *Ibid.*, **34**, 1006.

"urobilin" absorption band. Various unsuccessful attempts were made to precipitate the haemopyrrol mercury compound directly from the filtered solution, without distilling.

The filtrate from the mercury derivative gradually turns red on standing and the liquid then shows the "urobilin" absorption band. It is evident, therefore, that the haemopyrrol is not completely precipitated from solution by the mercuric chloride. This would also diminish the yield of haemopyrrol.

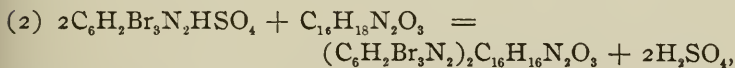
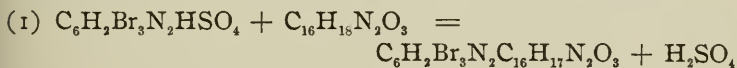
Some residues from the precipitation of bilirubin from chloroform by alcohol, which had a marked red color, though they may have contained some biliverdin and some of the compound more soluble in chloroform, were reduced according to the method described above. To 0.34 gram of the residue we used 3.4 grams of phosphorus and 27.2 grams of iodine and obtained a very light yellow solution. When this was partly neutralized with sodium carbonate, sodium acetate added and distilled in a current of carbon dioxide, the distillate gave a precipitate with mercuric chloride exactly like that resulting from the acethaemin. The liquid remaining in the flask also became dark colored—almost black—on standing and showed the "urobilin" spectrum. When the precipitate with the mercuric chloride solution was examined, it was found to be different from the haemopyrrol-mercuric chloride precipitate obtained from the acethaemin. Only a small part of it was soluble in alcoholic hydrochloric acid, whereas the haemopyrrol-mercuric chloride precipitate completely dissolves. The solution of the mercuric chloride compound in the alcoholic hydrochloric acid behaved exactly like that of the haemopyrrol-mercuric chloride compound, however, rapidly becoming colored and showing the "urobilin" spectrum. The amount of the precipitate was small and the greater part was evidently not the haemopyrrol-mercuric chloride derivative. Similar precipitates were obtained from pure bilirubin, from the compound more soluble in chloroform, from the green "biliverdin" and also from the "bilihumin," the residues in the Soxhlet thimble after extraction with chloroform. All these substances seem to yield small quantities of haemopyrrol on reduction. Bilirubin is much more resistant to the action of reducing agents than acethaemin.

5. Azo Compounds of Bilirubin.

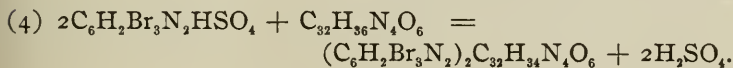
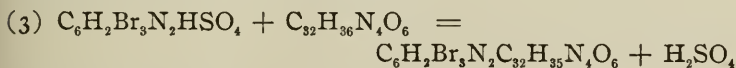
Ehrlich¹ found, in 1883, that benzenediazonium sulphonate reacts very readily with bilirubin, the product being red in neutral, weakly alkaline, or faintly acid solutions. With strong hydrochloric acid it is beautifully blue and in strong alkalies greenish-blue. None of the other pigments found in the bile gave this reaction. In 1900 Pröscher² combined bilirubin with acetophenonediazonium chloride and isolated the product, which he named acetophenoneazobilirubin.

As it was highly probable, from our work on the reduction of bilirubin, that it was a derivative of pyrrol, we expected to get here two compounds, a monazo and a disazo derivative, as O. Fischer and Hepp³ had found to be the case with pyrrol and its homologues. Investigation soon showed that this supposition was correct. By means of these compounds we hoped to be able to determine the molecular weight and formula of bilirubin.

Tribromaniline was the base selected from which to make the diazonium compound, as the amount of bromine which it contains is so large that it is very easy, by simply making a bromine determination, to distinguish between the monazo and the disazo derivatives. If the formula of bilirubin is $C_{16}H_{18}N_2O_3$, we should expect the tribromdiazonium salt to combine with it in accordance with the following equations:



while, if the molecule of bilirubin is represented by the formula $C_{32}H_{36}N_4O_6$, the equations would be:



¹ Z. anal. Chem., **23**, 275 (1883).

² Z. physiol. Chem., **29**, 411.

³ Ber. d. chem. Ges., **19**, 2251.

The formulas of the resulting compounds, their molecular weights and the percentages of bromine they contain are shown below :

	Formula.	Molecular weight.	Percentage of bromine.
1	$C_{22}H_{19}N_4O_3Br_3$	627.23	38.244
2	$C_{25}H_{20}N_6O_3Br_6$	968.16	49.55
3	$C_{33}H_{37}N_6O_6Br_3$	913.49	26.26
4	$C_{44}H_{38}N_8O_6Br_6$	1254.46	38.244

If the two azo compounds can be shown to contain 26.26 and 38.24 per cent of bromine respectively, then the formula of bilirubin must be $C_{32}H_{36}N_4O_6$. Compounds 1 and 4 contain the same amount of bromine and it is impossible to distinguish between them by analysis. The molecular weight of 4, however, is double that of 1.

The tribromaniline was made according to the method of Fritzsche, as given by Silberstein¹ and also by the one recommended by Jackson and Bancroft.² Both gave a product, which, when purified, melted at 119° and was free from other bromine derivatives of aniline as shown by analyses :

I. 0.3051 gram tribromaniline gave 0.5225 gram AgBr.

II. 0.1999 gram tribromaniline gave 0.3410 gram AgBr.

	Calculated for $C_6H_2Br_3NH_2$.	I.	Found. II.
Br	72.70	72.89	72.60

Analysis I. was made by the Carius method ; II. by heating with lime.

In the earlier experiments the tribromaniline was diazotized by means of nitrogen trioxide, according to Silberstein's directions, but after the publication of Hantzsch and Jochem's³ article, their much superior method was alone used. The tribrombenzenediazonium acid sulphate was beautifully crystallized and pure white. It was dried over sulphuric acid before use. After many trials, we found the following to be the best method of preparation of the azo compounds : dissolve about 2 grams of pure bilirubin, by heating with 800-900 cc. of chloro-

¹ J. prakt. Chem., [2], **27**, 100 (1883).

² THIS JOURNAL, **12**, 290 (1890).

³ Ber. d. chem. Ges., **34**, 3337 (1901).

form in a flask connected with a reflux condenser, cool the solution to 8° and add 250 cc. of absolute alcohol. Then dissolve about 3.5 grams of the *freshly* prepared tribrombenzenediazonium acid sulphate in 10–15 cc. of cold distilled water and add this solution to the first one, shake thoroughly, add more alcohol, if necessary, to make a homogeneous solution and allow to stand until the liquid has assumed the room temperature. The addition of the diazonium salt causes a marked change in color, the liquid finally becoming deep-red. Now add a large excess of distilled water; the chloroform separates, carrying with it the azo compounds, while the alcohol and the excess of the diazonium salt dissolve in the water; the latter is siphoned off and the chloroform washed repeatedly with large amounts of water in order to remove the alcohol. During this washing a precipitate gradually forms, consisting chiefly of the monazo product which was held in solution by the alcohol. The chloroform, after separation from the water, is filtered and shaken with about 500 cc. of 2 per cent potassium hydroxide solution to remove the azo compounds. A small amount of tribrombenzene, formed by the interaction of some of the tribrombenzene diazonium acid sulphate with the alcohol, remains in the chloroform. The potassium hydroxide solution of the azo compounds is separated from the chloroform and washed with some fresh chloroform to remove all the tribrombenzene; the azo compounds are then completely precipitated by adding slight excess of dilute sulphuric acid, washed with water by decantation, until the wash water is free from sulphates, filtered and dried. During the washing the wash waters remain nearly colorless until the sulphates are almost entirely removed, then a little of the azo compound seems to go into solution.

The large excess of diazonium salt used was for the purpose of combining with *all* the bilirubin and also because some of it is decomposed by the alcohol. It was hoped that, by the use of a large excess of diazonium salt, it would be possible to convert the bilirubin entirely into the disazo product. Some monazo compound was always formed, however, no matter how the conditions were varied. 1.1 grams of bilirubin gave 1.8 grams of the azo derivatives, consisting chiefly of the disazo product.

The separation of the two azo compounds is long and tedious. Ethyl acetate gave the best results. After several trials we adopted the following method: The powdered mixture of the azo compounds is placed in a paper thimble, in the Soxhlet apparatus and extracted with ethyl acetate (free from acetic acid) until soluble red compounds are removed. Most of the monazo compound remains and the greater part of the disazo compound dissolves. The extract is filtered, concentrated, and, on standing, some material separates which consists chiefly of the monazo compound; it is filtered and the evaporation continued, removing the monazo compound each time as it precipitates, until, finally, the material which separates consists chiefly of the disazo compound. It is easy to distinguish the monazo and disazo compounds, the former gives a red and the latter a beautiful purple color with potassium hydroxide.

The solution remaining is evaporated to dryness on the water-bath, the residue powdered and redissolved in as small an amount of ethyl acetate as possible, filtered, concentrated (the monazo product being removed as it separates) and finally evaporated to dryness. The whole process is then repeated until the residue dissolves *completely* in ethyl acetate. The product may then be recrystallized from ethyl acetate or precipitated from this solution by means of petroleum ether. In some cases we evaporated the ethyl acetate solution to dryness, dissolved the residue in 2 per cent potassium hydroxide, precipitated with dilute sulphuric acid, washed free from sulphates, filtered and dried.

The pure monazo compound is nearly insoluble in ethyl acetate, but in the presence of the disazo product a part of it always goes into solution. A fairly good separation can be effected by using chloroform, but as the monazo compound is more soluble in this than in the ethyl acetate, the separation is much slower and not so complete. The two azo compounds may also be separated by dissolving them in 2-3 per cent potassium hydroxide solution and passing excess of carbon dioxide. The disazo compound precipitates first leaving most

of the monazo compound in solution. Here again, however, the separation is not complete unless the process is repeated four or five times, as some of the disazo compound remains in the carbonate solution and some of the monazo product precipitates. Of the specimens finally obtained for analysis, No. 1 was purified by the ethyl acetate method, No. 2 by dissolving in 2 per cent potassium hydroxide and precipitating with carbon dioxide, repeating the process four times and using large volumes of alkali. The products were dried at 100°.

Analytical results :

I. 0.1348 gram substance gave 0.1202 gram AgBr (Carius).

II. 0.1070 gram substance gave 0.0954 gram AgBr, heating with lime.

0.1640 gram substance gave 10.31 cc. N/10 NH₃. Material first reduced by the Chenel method, then oxidized by the Kjeldahl-Gunning method.

	Calculated for $C_{32}H_{34}N_4O_6(C_6H_2Br_3N_2)_2$.	I.	Found. II.
Br	38.24	37.95	37.94
N	8.95	. .	8.83

An attempt was made to obtain measurable crystals of the disazo compound from glacial acetic acid, in which it is very soluble and from which it crystallizes beautifully, in large, well-formed rosettes, easily visible to the naked eye. The crystals were very dark, almost black, with a peculiar bronze luster. When dried, however, they lost weight steadily for a long time, even in the water-oven and the bromine determinations invariably came a little low. Whether this was due to the presence of acetic acid of crystallization, to the formation of acetyl compounds, or to loss of bromine we were unable to determine. From the slowness with which the compound lost weight we were inclined to regard it as an acetyl derivative of the disazo product. One specimen, dried to constancy at 112°, steadily decreased in weight during 50 hours and had then lost approximately the equivalent of 4 molecules of acetic acid to 1 of the disazo compound. This substance was analyzed.

I. 0.1228 gram substance gave 0.1048 gram AgBr. Percentage of bromine 36.31.

II. 0.1016 gram substance gave 0.0866 gram AgBr. Percentage of bromine 36.27.

These values show that the compound had lost bromine as well as acetic acid, or that all the acetic acid had not been removed. At higher temperatures the loss was greater and the dried product was changed in character, so that the work with it was discontinued. Even in the case of the *purest* products obtained from ethyl acetate there seemed to be a steady loss of bromine if the substance was heated for any length of time above 100°.

The other azo derivative, which we have called the monazo compound, was obtained by collecting the material precipitating out of the chloroform solutions of the mixed azo products, when these were washed with water, and also the substance deposited from the ethyl acetate solutions of the azo compounds during concentration. The mixture was powdered, placed in the paper thimble containing the azo product insoluble in ethyl acetate and the whole re-extracted with ethyl acetate. The extract was concentrated and any monazo compound which separated was collected and again extracted. This process was continued until a product was obtained almost insoluble in chloroform or ethyl acetate, more soluble in alcohol and soluble in dilute alkalis with a *red* color. When a specimen dissolved in alkalis with a pure red color, the solution giving no absorption band,¹ it was assumed to be pure and free from the disazo derivative, as we found it impossible to crystallize it from any solvent. Some of the preparations seemed to be contaminated with a product containing a smaller amount of bromine, possibly a decomposition-product of the monazo compound itself; this could be partially removed by extracting the substance with alcohol, but, if the extraction were continued too long, the monazo compound was dissolved

¹ As will be shown later, the *disazo* compound gives a very marked and characteristic absorption band in acid or alkaline solution, while the monazo product gives none.

and, in any case, there was considerable loss of the latter by this method of purification. The total amount of monazo product which we obtained was small and we were therefore not able to purify it perfectly. Analyses of specimens dried at 105° :

I. 0.0950 gram substance gave 0.0567 gram AgBr. Heating with lime.

II. 0.0814 gram substance gave 0.0486 gram AgBr (Carius).

	Calculated for $C_{32}H_{35}N_4O_6(N_2C_6H_2Br_3)$.	I.	Found. II.
Br	26.26	25.40	25.41

These results show that the compound must be a monazo derivative, having the formula $C_{32}H_{35}N_4O_6(N_2C_6H_2Br_3)$ and hence that the formula of bilirubin itself must be $C_{32}H_{36}N_4O_6$.

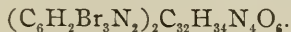
Some products were obtained which gave a higher percentage of bromine, but an examination of their alkaline solutions showed the absorption band so characteristic of the disazo product, hence these analyses were discarded.

Several attempts were made to prepare the monazo compound by mixing bilirubin with the calculated amount of tribrombenzenediazonium salt, but without success, as a mixture of the two azo derivatives was always formed. Even when we mixed 10 cc. of concentrated hydrochloric acid with the chloroform-alcohol solution of 2 grams of bilirubin, before the solution of the diazonium salt was added, the result was the same. We also endeavored to make the disazo compound exclusively, by allowing the diazonium salt to remain in contact with the bilirubin solution over night, but here again a mixture of the two azo compounds was always obtained.

The results from the analyses of the disazo product agree just as well with the formula for the monazo derivative,



(see p. 238) as they do for that of the disazo compound,



That this product is a disazo compound, however, seems to be proved from the following considerations:

1. It gives a fine blue color with concentrated hydrochloric or sulphuric acid, the monazo compound gives a red color with these reagents. This is in accord with the statements made by O. Fischer and E. Hepp regarding the conduct of disazo and monazo compounds of pyrrol and its homologues towards strong acids.

2. The fact that this product is formed in largest quantity when an *excess* of the diazonium salt is present, is also an indication that it is a disazo and not a monazo compound.

3. We made many unsuccessful attempts to isolate a product from the mixture of the azo compounds containing more bromine than this one.

As will be seen from the table on p. 238, if the disazo compound has the formula $(C_6H_2Br_3N_2)_2C_{16}H_{16}N_2O_3$, the percentage of bromine would be 49.55, whereas the highest percentage we found in any azo compound was only 37.95. Moreover, as shown above, by the action of tribromobenzenediazonium acid sulphate on bilirubin we obtained an azo compound which contains 25.4 per cent of bromine, dissolves in concentrated hydrochloric or sulphuric acid with a red color and which must, therefore, be the monazo compound,



As the disazo compound is fairly soluble in chloroform and in ethylacetate, we endeavored to confirm, by molecular weight determinations, the view of its composition given above, using the Landsberger-McCoy apparatus:

Solvent, Chloroform.

Disazo product. Grams.	Solution. cc.	Rise in boiling-point.	Molecular weight found.	Molecular weight calculated for $C_{32}H_{34}N_4O_6(C_6H_2Br_3N_2)_2$.
1.15 (742-741.2 mm.)	11.2	0°.207	1289	1254.46
	13.9	0°.147	1463	
	17.8	0°.130	1292	
	19.3	0°.135	1148	
0.9763	8.6	0°.207	1426	
				For $C_{16}H_{17}N_2O_3(C_6H_2Br_3N_2)$.
746 mm.)	12.1	0°.153	1371	627.23
	16.3	0°.122	1276	
	23.8	0°.086	1240	
0.526 (747-746.9 mm.)	11.8	0°.079	1467	

Solvent Ethyl Acetate.

Disazo product. Grams.	Solution. cc.	Rise in boiling-point.	Molecular weight found.
0.2675 (Bar. 742 mm.)	8.4	0.096	1042

These values indicate that the disazo compound has a molecular weight of 1254.46, which corresponds to the formula $C_{32}H_{34}N_4O_6(C_6H_2Br_3N_2)_2$. Bilirubin itself must, then, have the formula $C_{32}H_{36}N_4O_6$.

Owing to the very high molecular weight of the disazo compound and the great difficulty of dissolving it, as well as its slight solubility in the solvents used, we do not lay too much stress on these molecular weight determinations; they are recorded, however, just as they were made and the results agree with those obtained from the analyses of the azo compounds. Attention should, perhaps, be called to the fact that these conclusions are in accord with Maly's on tri-brombilirubin,¹ hydrobilirubin and on the oxidation of bilirubin to biliverdin and also with Abel's determinations of the molecular weight of hydrobilirubin² by the cryoscopic method.

According to measurements made for us by Mr. L. F. Hawley, the disazo compound, in alcoholic potassium hydroxide solution, gave a well-defined absorption band between $\lambda = 606$ and $\lambda = 536$. In alcoholic hydrochloric acid the band was between $\lambda = 573.5$ and $\lambda = 495.5$. The latter is weaker and not so well defined as the former.

The following table shows the differences observed between the two azo compounds:

	Disazo compound, $C_{32}H_{34}N_4O_6(C_6H_2Br_3N_2)_2$.	Monazo compound, $C_{32}H_{36}N_4O_6(C_6H_2Br_3N_2)$.
Potassium hydroxide (2 per cent)	Bluish purple	Red
Concentrated hydro- chloric acid	" "	Purplish-red
Acids or alkalies	Absorption band	No absorption band
Chloroform	Very soluble	Slightly soluble
Ethyl acetate	Soluble	Insoluble
Carbon disulphide	"	"
KOH solution + CO_2	Precipitates	Remains in solution

¹ Jahresber. u. die Fortsch. der Thierchemie, 5, 193.

² Monats. Chem., 11, 61 (1890).

In neutral or ammoniacal solution the disazo compound is red and these solutions show no absorption band.

Azo Compounds Formed from Bilirubin with Diazonium Acetophenone Salts.

As has already been stated, Pröscher combined bilirubin with acetophenone diazonium chloride and obtained a compound, crystallizing from chloroform, to which he assigned the formula $C_{24}H_{25}N_4O_4$.

After we discovered that tribrombenzenediazonium acid sulphate combines with bilirubin to form a monazo and a disazo derivative, we decided to repeat Pröscher's work. The method used in making the azo compounds was the same as that employed in making the tribrommonazo and disazo products given above, differing from Pröscher's only in that the acetophenone diazonium acid sulphate was made by Hantzsch and Jochem's method and that it was isolated and purified before use. We found that two azo compounds are also formed here, one, the monazo, not very soluble in chloroform and practically insoluble in carbon disulphide, the other, the disazo derivative, analyzed by Pröscher, quite soluble in these media. Some of the data given by Pröscher differ slightly from ours.

Carbon disulphide is the best solvent for the separation of the two azo compounds. The mixture was extracted in a Soxhlet apparatus with carbon disulphide until the solvent runs off practically colorless. Part of it was then distilled; on cooling, crystals of the disazo compound separated. More crystals were obtained by further evaporation. These were collected and re-extracted with carbon disulphide. Two or three extractions and crystallizations are sufficient to obtain a pure product. After recrystallizing from carbon disulphide three times, thin, shining crystals, 1-2 mm. in length, were obtained. These were described by Professor A. C. Gill, of the Mineralogical Department of Cornell University, as follows: "The substance crystallizes in elongated, wedge-shaped plates, which are frequently aggregated into rosette-like forms, red by transmitted light, somewhat pleochroic, with purplish and yellowish tinges to the red; oblique

extinction showing that they are either monoclinic or triclinic. In converged polarized light they show that the tabular faces are not at right angles to any axis of elasticity, hence the crystals are probably triclinic." Another portion, obtained in a similar manner, was described by Dr. Gill as follows: "The groups of yellowish-red to brownish-red, thin, tabular crystals are doubtless triclinic and show pleochroism. An optical axis seems to emerge at a small angle with the normal to the flat face."

Analyses of the product, recrystallized three times from carbon disulphide and dried to constant weight in a water-oven:

I. 0.1599 gram substance gave 19 cc. N at 19° and 739.6 mm. (cor.)

II. 0.0919 gram substance gave 8.49 cc. N/10 NH₃.

N	Calculated for $C_{32}H_{34}N_4O_6(C_8H_7N_2O)_2$.	Found.	
		I.	II.
	12.99	13.29	12.97

Analysis I. was made by the Dumas method; II. by first reducing the compound with phosphorus and iodine (Chenel) and then oxidizing with sulphuric acid and potassium sulphate (Kjeldahl-Gunning method).

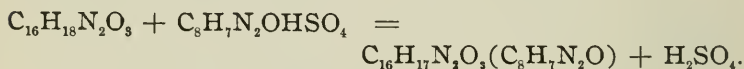
The results show that the compound is identical with Pröscher's product.

The monazo compound, insoluble in carbon disulphide and only slightly soluble in chloroform, was exhaustively extracted with these solvents until it was free from the disazo product. This point was quite readily determined by dissolving the monazo compound in alcohol, adding some potassium hydroxide and examining the solution with the spectroscope. The slightest trace of the disazo compound may be detected by the very marked absorption band. When the monazo compound was freed from the disazo product it was dissolved in alcohol, filtered and evaporated to dryness on the water-bath. Only a small quantity of the pure monazo compound was obtained. Its alcoholic solution is red and turns bluish-green on the addition of alkalis; in strong hydrochloric acid the color is deep purple. Analysis of this product, dried to constant weight at 100° (Chenel-Kjeldahl method):

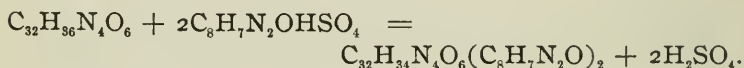
0.0535 gram substance gave 4.56 cc. N/10 NH_3 .

	Calculated for $\text{C}_{32}\text{H}_{35}\text{N}_4\text{O}_6(\text{C}_8\text{H}_7\text{N}_2\text{O})$.	Found.
N	11.72	11.96

This result shows that the compound is a monazo derivative and that the one analyzed by Pröscher must, therefore, be the disazo compound; he gives it the formula $\text{C}_{24}\text{H}_{25}\text{N}_4\text{O}_4$, but this is certainly wrong. Even if we assume the formula, $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_3$, for bilirubin, the product resulting from the action of the acetophenone diazonium acid sulphate would have the formula $\text{C}_{24}\text{H}_{24}\text{N}_4\text{O}_4$, as shown in the following equation:



As the formula for bilirubin is undoubtedly $\text{C}_{32}\text{H}_{36}\text{N}_4\text{O}_6$, the derivative is certainly a disazo compound and the equation representing the reaction is as follows:



We give below the results obtained by Pröscher and those required by our formula. We have recalculated Pröscher's values ($\text{O} = 16$).

	Calculated for $\text{C}_{32}\text{H}_{34}\text{N}_4\text{O}_6(\text{C}_8\text{H}_7\text{N}_2\text{O})_2$.	Pröscher's results.
C	66.61	66.17
H	5.60	6.04
N	12.99	12.97

The disazo compound dissolves in alkali, forming a clear blue solution, which gradually changes to green, then to yellow and finally becomes nearly colorless. Pröscher states that his substance dissolved in alkalies with a green color. Neutral and acetic acid solutions of the disazo product are red, those in concentrated hydrochloric or sulphuric acid are purple or blue, depending on the amount of acid and pigment present.

We obtained almost exactly the same absorption bands as those recorded by Formanek,¹ though we could not pretend to read the maximum points as sharply as he does. We used a

¹ Z. physiol. Chem., 29, 414 (1900).

grating and zirconia light. In alcohol we observed one band with maximum darkness at about $\lambda = 522$; Formanek gives $\lambda = 524.9$. Addition of concentrated hydrochloric acid to the alcoholic solution gives two bands, with a lighter space between, at about $\lambda = 539$; Formanek gives $\lambda = 561.4$ and $\lambda = 525.8$. In alcoholic potassium hydroxide, according to a determination made for us by Dr. Benton Dales, a very marked band is shown with a maximum darkness at $\lambda = 639$; Formanek gives $\lambda = 643.1$.

Substances more Soluble in Chloroform.

Küster has reserved the investigation of the substances in ox-gallstones, which resemble bilirubin very closely, but are more soluble in chloroform and contain less nitrogen, consequently no attempt at a careful study of them was made. In crystallizing crude bilirubin from chloroform, the more soluble products, accumulated in the mother-liquors, may be obtained by evaporation or by precipitation with petroleum ether. Carbon disulphide, methyl alcohol, ethyl alcohol, ethyl acetate, acetone, benzene, toluene and ether all dissolve some of the material and, on concentration, it separates in imperfect micro-crystalline masses. Chloroform is the best solvent.

About 1.5 grams of the material were dissolved in a mixture of chloroform and benzene and the solvent gradually evaporated. At a concentration of about 200 cc., when most of the chloroform had volatilized, a considerable amount of red micro-crystalline substance separated. This was removed; further concentration of the mother-liquor gave a similar precipitate, very much darker in color. Analyses (Chenel-Kjeldahl):

- I. 0.1406 gram of the red product gave 9.39 cc. N/10 NH_3 .
- II. 0.1940 gram of the dark product gave 10.31 cc. N/10 NH_3 .

	I.	II.
N	9.38	7.46

Summary.

1. Analyses of the *pure crystallized* bilirubin show that its

composition is correctly represented by the formula $(C_{16}H_{18}N_2O_3)_x$.

2. Bilirubin unites with diazonium compounds, in acid or neutral solutions, forming monazo and disazo derivatives.

3. The monazo compounds have the formula $C_{32}H_{35}N_4O_6(N_2R)$. They are formed in much smaller quantity than the disazo products, are more readily soluble in alkalies and are not precipitated by carbon dioxide. Their solutions show no absorption bands. In most neutral solvents, like carbon disulphide, chloroform and ethyl acetate, they are less soluble than the disazo products.

4. The disazo compounds have the formula $C_{32}H_{34}N_4O_6(N_2R)_2$. They are soluble in alkalies and are precipitated by carbon dioxide. Their solutions show characteristic absorption bands.

5. The existence of these two series of azo derivatives shows that the molecular formula for bilirubin must be $C_{32}H_{36}N_4O_6$.

6. Molecular weight determinations of the tribrombenzene-disazobilirubin are in accord with the results of the analyses of the azo compounds and show that this substance has the formula $C_{32}H_{34}N_4O_6(N_2C_6H_2Br_3)_2$, hence, that the formula of bilirubin is $C_{32}H_{36}N_4O_6$.

7. Bilirubin has acid properties similar to those of the phenols. It is precipitated from alkaline solution by carbon dioxide. It contains no alkyloxy group and probably no alkyl-imide group. It does not reduce ammoniacal silver nitrate solution, even on boiling, so probably does not contain an aldehyde group. It resembles resorcinol very closely in the manner in which it forms monazo and disazo derivatives.

8. When reduced by zinc dust or nascent hydriodic acid, bilirubin gives haemopyrrol, showing that it is a derivative of pyrrol. The ease with which it forms monazo and disazo compounds, even in the presence of strong acids, points to the same conclusion.

CORNELL UNIVERSITY,
ITHACA, N. Y.,
May, 1904.

XLV.—ON THE COMPOSITION OF PETROLEUM.¹

BY CHARLES F. MABERY.

I. THE HYDROCARBONS IN OHIO TRENTON LIMESTONE PETROLEUM.

BY CHARLES F. MABERY AND O. H. PALM.

II. THE HYDROCARBONS IN CANADIAN PETROLEUM WITH HIGH BOILING-POINTS.

III. HYDROCARBONS IN SANTA BARBARA CRUDE OIL.

IV. SEPARATION OF SOLID PARAFFIN HYDROCARBONS FROM PETROLEUM WITHOUT DISTILLATION.

BY CHARLES F. MABERY AND OTTO J. SIEPLEIN.

V. THE SOLID PARAFFIN HYDROCARBONS THAT COLLECT IN OIL WELLS IN PENNSYLVANIA.

VI. COMPOSITION OF COMMERCIAL PARAFFIN.

VII. COMPOSITION OF COMMERCIAL VASELINE, COSMOLINE, AND SIMILAR PRODUCTS.

I. THE HYDROCARBONS IN OHIO TRENTON LIMESTONE PETROLEUM WITH BOILING-POINTS ABOVE 213°.

With O. H. PALM.

In a paper on the constituents of Pennsylvania, Ohio and Canadian petroleum with boiling-points between 150° and 220°, ² it was shown, as a result of combustion, molecular weight determinations and composition of its chlorine derivatives, that the distillate boiling at 212°–214° from Ohio Trenton limestone petroleum consisted of hendecane, C₁₂H₂₆. Study of the portions with higher boiling-points has since been continued for the purpose of ascertaining where the series C_nH_{2n+2} terminates and the series poorer in hydrogen appears.

The higher specific gravity of Trenton limestone petroleum and of the products prepared from it is well known, but the

¹ Aid in this work was given by the American Academy of Arts and Sciences from the C. M. Warren Fund for Chemical Research.

² THIS JOURNAL, 19, 419 (1897).

cause has not yet been explained. Since the series C_nH_{2n+2} has been found to continue, in Pennsylvania petroleum, in the solid forms as high as their molecular weights can be determined and to be associated with series poorer in hydrogen above 260° (50 mm.), it was evidently interesting to ascertain the composition of the higher hydrocarbons in Ohio oil.

Results which will appear later show that the series poorer in hydrogen form the chief portion of Canadian petroleum; and since the Trenton limestone oil, in its physical properties and in the properties of its distillates, stands in an intermediary position between Pennsylvania and Canadian crude oils, the series of hydrocarbons in Ohio oil should explain the difference in properties of the commercial products obtained from it.

In resuming the study of Ohio Trenton limestone oil in 1901, a barrel of the crude oil was obtained at Welker, Ohio, of sp. gr. 0.8367 at 20° . Analysis gave: C 85.46; H 13.91; S 0.48 per cent.

This crude oil is not so heavy as some specimens from Lima and Indiana and the percentage of sulphur is lower than that of specimens from some other fields, but it was believed to represent an average composition of Trenton limestone oil with reference to the principal series of hydrocarbons.

From 8 liters of the crude oil 1.8 liters were removed, below 200° , under atmospheric pressure; the residue was distilled under 30 mm., at first within limits of 10° , which left a residue, above 280° , of 2,000 grams. Subsequent distillation, under the same pressure, brought the distillates together in larger quantities, within certain well-defined limits of temperature, indicating a greater proportion of individual hydrocarbons. After ten distillations, greater amounts collected within the following limits, and were found to represent definite compounds: 111° – 113° ; 129° – 130° ; 138° – 140° ; 152° – 154° ; 164° – 168° ; 177° – 179° ; 187° – 190° ; 198° – 202° ; 213° – 216° ; 224° – 227° ; 237° – 240° ; 253° – 255° ; 263° – 265° ; 275° – 278° . Although it cannot be assumed that, in a limited number of distillations, the individual hydrocarbons can be separated completely, analysis and molecular weight determinations indicate that the separation is suffi-

cient to admit of identification, not only of members of the same series but of rather sudden changes from one series to the next poorer in hydrogen.

None of the fractions showed evidence of decomposition. The lower fractions were liquid, but the distillate 213° – 217° was nearly solid at ordinary temperatures. The higher distillates were completely solid with paraffin, which formed a large part of these fractions. Since the solid hydrocarbons in Pennsylvania petroleum were identified as members of the series C_nH_{2n+2} , and the solid hydrocarbons in Ohio petroleum are, without doubt, composed of the same bodies, it was considered unnecessary to examine these solids from Ohio oil. To remove them the oil was cooled to 0° , filtered, then cooled to -10° and again filtered, under pressure, at the same temperature. In the higher distillates the solid hydrocarbons formed one-third or one-half of each distillate. The oils filtered from these fractions were very thick and viscous; the specific gravity of the unpurified fractions, at 20° , were found to be essentially higher than the corresponding fractions from Pennsylvania oil:

129° – 130° .	138° – 140° .	152° – 154° .	177° – 179° .	187° – 190° .	198° – 202° .
0.7998	0.8065	0.8187	0.8262	0.8351	0.8373
	224° – 227° .	237° – 240° .	253° – 255° .	275° – 278° .	
(At 50°)	0.8586	0.8622	0.8849	0.8941	

After removal of the solid hydrocarbon each fraction was thoroughly purified by agitating, first with common concentrated and then with fuming sulphuric acid until the latter was nearly colorless. The heavier distillates were dissolved, before treatment, in light gasoline; otherwise they formed an emulsion with acid from which the oil did not readily separate. To completely remove the acid the oil was finally washed with sodium hydroxide, then dried over calcium chloride and finally over sodium. If the oil remains unchanged after standing some time over sodium it is very well purified.

In the present state of our knowledge concerning the series of hydrocarbons poorer in hydrogen than the series C_nH_{2n+2} , definite names cannot be assigned to the members of these series. It is probable that the series C_nH_{2n} is composed of the

methylene hydrocarbons, perhaps with complex side chains. The series still poorer in hydrogen may contain two or more methylene rings, but as yet there is no evidence as to the structure of these hydrocarbons.

Hydrocarbon $C_{12}H_{24}$, *B. P.* 211° – 213° .—In a former paper¹ the fraction 212° – 214° , under atmospheric pressure, was shown by analysis and further identification to be dodecane $C_{12}H_{26}$, and its sp. gr. was found to be 0.7727 at 20° . This hydrocarbon was separated, with others, from a specimen of crude oil obtained from a well at Findlay, Ohio. Its sp. gr. and composition corresponded to that of dodecane, which was obtained from Pennsylvania petroleum.

The fraction 211° – 213° , now under examination, after thorough purification with sulphuric acid, as described above, gave sp. gr. 0.7970.

I. 0.1462 gram oil gave 0.4590 gram CO_2 and 0.1860 gram H_2O .

II. 0.1281 gram oil gave 0.4020 gram CO_2 and 0.1635 gram H_2O .

III. 0.1563 gram oil gave 0.4906 gram CO_2 and 0.2000 gram H_2O .

	Calculated for C_nH_{2n} .	I.	Found. II.	III.
C	85.70	85.62	85.53	85.61
H	14.30	14.25	14.27	14.31

The molecular weight, determined by Beckmann's freezing-point method, in benzene, agreed with that of the formula $C_{12}H_{24}$.

1.1097 grams oil and 29.394 grams benzene gave a depression of $1^{\circ}.067$.

Calculated for $C_{12}H_{24}$.	Found.
168	173

The same formula was verified by the index of refraction, 1.4350, from which the molecular refraction was calculated.

Calculated for $C_{12}H_{24}$.	Found.
54.24	55.00

¹ *Loc. cit.*

It is, therefore, evident that this hydrocarbon has the composition of the series C_nH_{2n} . The only explanation that can be offered as to the difference between it and the product with the same boiling-point separated before, is that the different specimens of oils, coming from different sources, must have differed with respect to this hydrocarbon.

Hydrocarbon $C_{13}H_{26}$, B. P. 123° – 125° (30 mm.).—After ten distillations under 30 mm., 27 grams collected at 129° – 130° , that distilled, under atmospheric pressure, at 223° – 225° . After careful purification the sp. gr. of this distillate was found to be 0.8055 at 20° . It was shown to belong to the series C_nH_{2n} .

I. 0.1536 gram oil gave 0.4824 gram CO_2 and 0.1902 gram H_2O .

II. 0.1336 gram oil gave 0.4195 gram CO_2 and 0.1710 gram H_2O .

	Calculated for $C_{13}H_{26}$.	I.	Found. II.
C	85.70	85.65	85.63
H	14.30	13.85	14.32

The molecular weight, determined at the freezing-point of benzene, corresponded to the formula $C_{13}H_{26}$.

0.9896 gram oil and 25.6727 grams benzene gave a depression of $1^\circ.040$.

Calculated for $C_{13}H_{26}$.	Found.
182.0	181.6

A determination of the index of refraction gave 1.4400, which corresponded to the molecular refraction :

Calculated for $C_{13}H_{26}$.	Found.
59.84	59.55

Hydrocarbon $C_{14}H_{28}$, B. P. 138° – 140° (30 mm.).—After the tenth distillation 45 grams, collected at 138° – 140° , gave sp. gr. 0.8129, at 20° , after thorough purification with acid.

0.1407 gram oil gave 0.4435 gram CO_2 and 0.1787 gram H_2O .

	Calculated for $C_{14}H_{28}$	Found.
C	85.70	85.96
H	14.30	14.18

The formula was verified by the molecular weight, at the freezing-point of benzene.

0.9552 gram oil and 24.5822 grams benzene gave a depression of $0^{\circ}.975$.

	Calculated for $C_{14}H_{28}$	Found.
	196	195.2

The index of refraction was found to be 1.4437 and the molecular refraction agreed with the same formula :

	Calculated for $C_{14}H_{28}$	Found.
	64.44	64.10

Hydrocarbon $C_{15}H_{30}$, *B. P.* 152° – 154° (30 mm.).—A fraction of 75 grams, collected at first within these limits, gradually diminished to 20 grams after the tenth distillation. After purification with acid it gave sp. gr. 0.8204 at 20° . Analysis gave values required for the series C_nH_{2n} :

0.1511 gram oil gave 0.4750 gram CO_2 , and 0.1920 gram H_2O .

	Calculated for $C_{15}H_{30}$	Found.
C	85.70	85.74
H	14.30	14.21

The molecular weight, determined at the freezing-point of benzene, corresponded to the formula $C_{15}H_{30}$.

0.9370 gram oil and 24.2115 grams benzene gave a depression of $0^{\circ}.910$.

	Calculated for $C_{15}H_{30}$	Found.
	210	208.3

This formula was further confirmed by the index of refraction, 1.4480, which gave the following molecular refraction :

	Calculated for $C_{15}H_{30}$	Found.
	69.05	68.50

Hydrocarbon $C_{16}H_{32}$, *B. P.* 164° – 168° (30 mm.).—Eighteen grams of the oil collected within these limits after the tenth distillation that gave sp. gr. 0.8249 at 20° . After filtration at -10° , and purification with acid, the sp. gr. was found to be 0.8254. The proportions of carbon and hydrogen indicated the series C_nH_{2n} .

0.1536 gram oil gave 0.4848 gram CO_2 and 0.1945 gram H_2O .

	Calculated for $C_{16}H_{32}$.	Found.
C	85.70	86.08
H	14.30	14.16

The molecular weight, at the freezing-point of benzene, corresponded to the formula $C_{16}H_{32}$.

1.1300 grams oil and 20.3767 grams benzene gave a depression of $1^{\circ}.202$.

Calculated for $C_{16}H_{32}$.	Found.
224	226

The index found, 1.4510, confirmed the same formula :

Calculated for $C_{16}H_{32}$.	Found.
73.65	73.08

Hydrocarbon $C_{17}H_{34}$, *B. P.* 177° – 179° (30 mm.).—After the tenth distillation 35 grams collected within these limits with sp. gr. 0.8251 at 20° . After filtration at -10° and treatment with acid the sp. gr. was 0.8335. The percentages of carbon and hydrogen indicated the series C_nH_{2n} .

0.1501 gram oil gave 0.4720 gram CO_2 and 0.1881 gram H_2O .

	Calculated for $C_{17}H_{34}$.	Found.
C	85.70	85.76
H	14.30	14.02

The molecular weight, at the freezing-point of benzene, agreed with the formula $C_{17}H_{34}$.

1.0880 grams oil and 24.9900 grams benzene gave a depression of $0^{\circ}.896$.

Calculated for $C_{17}H_{34}$.	Found.
238	238

The index of refraction, 1.4545, supported the same formula :

Calculated for $C_{17}H_{34}$.	Found.
78.25	77.50

A fraction collected at 188°–190° which should contain the next homologous hydrocarbon $C_{18}H_{36}$; the oil was unfortunately lost by an accident during filtration from the solid.

Hydrocarbon $C_{19}H_{38}$, B. P. 198°–202° (30 mm.).—Thirty grams of this fraction were collected after the tenth distillation, which gave sp. gr. 0.8364 at 20°. On cooling to –10° and filtration, 16 grams of the filtered oil were obtained with sp. gr. 0.8471 at 20°. Determinations of carbon and hydrogen indicated a change from the series C_nH_{2n} to the series C_nH_{2n-2} .

0.1528 gram oil gave 0.4830 gram CO_2 and 0.1845 gram H_2O .

	Calculated for $C_{19}H_{38}$.	Found.
C	86.36	86.24
H	13.64	13.52

A determination of the molecular weight, at the freezing-point of benzene, gave the formula $C_{19}H_{38}$.

0.9063 gram oil and 24.1120 grams benzene gave a depression of 0°.700.

Calculated for $C_{19}H_{38}$.	Found.
264	263

This formula was further verified by its index of refraction, which was found to be 1.4614, corresponding to the molecular refraction :

Calculated for $C_{19}H_{38}$.	Found.
85.35	85.57

Hydrocarbon $C_{21}H_{40}$, B. P. 213°–217° (30 mm.).—The hy-

drocarbon $C_{20}H_{38}$ was apparently absent, as the distillates were small and did not accumulate below 213° , at which point a larger amount was collected that proved to be the hydrocarbon $C_{21}H_{40}$. After the tenth distillation 25 grams gave sp. gr. 0.8417 at 20° . After filtration at -10° the sp. gr. was 0.8546 at 20° . The carbon and hydrogen corresponded to the series C_nH_{2n-2} .

0.1362 gram oil gave 0.4330 gram CO_2 and 0.1675 gram H_2O .

	Calculated for $C_{21}H_{40}$.	Found.
C	86.30	86.70
H	13.70	13.66

A determination of the molecular weight, at the freezing-point of benzene, gave a value required for the formula $C_{21}H_{40}$.

1.1020 grams oil and 25.1400 grams benzene gave a depression of $0^{\circ}.734$.

	Calculated for $C_{21}H_{40}$.	Found.
	292	292.6

The index of refraction found, 1.465, confirmed the same formula:

	Calculated for $C_{21}H_{40}$.	Found.
	94.56	94.45

Hydrocarbon $C_{22}H_{42}$, B. P. 224° – 227° (30 mm.).—After the tenth distillation 22 grams collected at 224° – 227° , the sp. gr. of which was 0.8480 at 20° . After filtration at -10° and treatment with acid in gasoline solution, the sp. gr. was 0.8614. The percentages of carbon and hydrogen were those required for the series C_nH_{2n-2} .

I. 0.1403 gram oil gave 0.4438 gram CO_2 and 0.1670 gram H_2O .

II. 0.1571 gram oil gave 0.4970 gram CO_2 and 0.1901 gram H_2O .

	Calculated for $C_{22}H_{42}$.	I.	Found.	II.
C	86.25	86.27		86.27
H	13.75	13.31		13.53

The molecular weight, determined at the freezing-point of benzene, corresponded to the formula $C_{22}H_{42}$.

0.8385 gram oil and 21.6023 grams benzene gave a depression of $0^{\circ}.602$.

Calculated for $C_{22}H_{42}$.	Found.
306	309

This formula was further confirmed by the molecular weight, determined at the boiling-point of benzene, which gave 310.

The index of refraction, 1.4690, supported the same formula, as shown by the corresponding molecular refraction :

Calculated for $C_{22}H_{42}$.	Found.
99.16	99.60

Hydrocarbon $C_{24}H_{46}$, B. P. 237° – 240° (30 mm.).—The hydrocarbon $C_{23}H_{44}$ did not appear in the small amounts of distillates between 227° and 235° . Within the limits 237° – 240° (30 mm.), 40 grams collected, which was solid with paraffin at ordinary temperatures. After filtration at -10° the thick, viscous oil gave sp. gr. 0.8639. The percentages of carbon and hydrogen were those required for the series C_nH_{2n-2} .

0.1515 gram oil gave 0.4804 gram CO_2 and 0.1855 gram H_2O .

	Calculated for $C_{24}H_{46}$.	Found.
C	86.23	86.48
H	13.77	13.70

The molecular weight, determined at the freezing-point of benzene, gave the value required for $C_{24}H_{46}$.

1.0900 grams oil and 28.0340 grams benzene gave a depression of $0^{\circ}.570$.

Calculated for $C_{24}H_{46}$.	Found.
334	334

With hydrocarbons of such high molecular weights, the limits of accuracy are reached in determinations by the cryoscopic method with the aid of solvents commonly used, on account of the slight depression of the freezing-point.

A determination of the index of refraction gave 1.4715, which corresponds to the molecular refraction of $C_{24}H_{46}$.

Calculated for $C_{24}H_{46}$.	Found.
108.4	108

Several higher fractions were collected at points where the oil showed a tendency to accumulate and the results of analysis indicated a series still poorer in hydrogen, C_nH_{2n-4} . Twenty-five grams of the oil collected at 253°–255°, from which the solid was separated by filtration at –10° and the heavy viscous oil was purified by sulphuric acid in gasoline solution; sp. gr. of the purified oil was 0.8842 at 20°. The values for carbon and hydrogen were those required for the series C_nH_{2n-4} .

0.1424 gram oil gave 0.4511 gram CO_2 and 0.1718 gram H_2O .

	Calculated for $C_{23}H_{42}$.	Found.
C	86.79	86.42
H	13.21	13.49

Several attempts to determine the molecular weight of this hydrocarbon by the freezing-point method failed, on account of the slight depression and the amount of oil was not sufficient for a determination by the boiling-point method. The index of refraction was found to be 1.4797, which corresponds to the following molecular weight:

Calculated for $C_{23}H_{42}$.	Found.
101.7	162.1

A fraction that collected in considerable quantity at 263°–265° (30 mm.), after treatment with sulphuric acid in gasoline solution and filtration at –10°, gave sp. gr. 0.8864 at 20°. The percentages of carbon and hydrogen were as follows:

0.1470 gram oil gave 0.4670 gram CO_2 and 0.1752 gram H_2O .

	Calculated for $C_{24}H_{44}$.	Found.
C	86.75	86.68
H	13.25	13.32

The molecular weight of this hydrocarbon was not determined for the same reasons as the preceding one. A determination of the index of refraction gave 1.4802, corresponding to the molecular refraction :

Calculated for $C_{24}H_{44}$.	Found.
106.5	106.3

A fraction of 40 grams, collected at 275° – 278° (30 mm.), was filtered at -10° and the thick viscous oil purified with acid. It gave sp. gr. 0.8912 at 20° and percentages of carbon and hydrogen required for the series C_nH_{2n-4} .

0.1547 gram oil gave 0.4914 gram CO_2 and 0.1814 gram H_2O .

	Calculated for $C_{25}H_{46}$.	Found.
C	86.71	86.66
H	13.29	13.11

The molecular weight of this hydrocarbon was not determined. The index of refraction was found to be 1.4810 and the molecular refraction as follows :

Calculated for $C_{25}H_{46}$.	Found.
110.9	110.5

While the precise formulas of the last three hydrocarbons are not determined with as complete data as those preceding, it is evident that the series C_nH_{2n-4} is established.

Ohio petroleum is, therefore, composed chiefly of the series C_nH_{2n+2} , C_nH_{2n} , C_nH_{2n-2} , and C_nH_{2n-4} . It resembles Pennsylvania petroleum in the large proportion of solid paraffin hydrocarbons; but the greater portion of the fractions boiling above 216° consists of the series C_nH_{2n} , which, together with the series poorer in hydrogen, explains the higher specific gravity of the crude oil and distillates prepared from it. It is probable that series still poorer in hydrogen are contained in the less volatile portions that cannot be distilled without decomposition.

The following table gives a summary of the hydrocarbons described in this paper, with their boiling-points and specific gravity at 20° :

Hydrocarbons Separated from Ohio Trenton Limestone Petroleum.

Series.	Formula.	Boiling-point.		Sp. gr. at 20°.
C_nH_{2n}	$C_{12}H_{24}$	211°-213°	atm. pressure	0.7970
"	$C_{13}H_{26}$	223°-225°	"	0.8055
"	$C_{14}H_{28}$	138°-140°	30 mm.	0.8129
"	$C_{15}H_{30}$	152°-154°	"	0.8204
"	$C_{16}H_{32}$	164°-168°	"	0.8254
"	$C_{17}H_{34}$	177°-179°	"	0.8335
C_nH_{2n-2}	$C_{19}H_{36}$	198°-202°	"	0.8364
"	$C_{21}H_{40}$	213°-217°	"	0.8417
"	$C_{22}H_{42}$	224°-227°	"	0.8614
"	$C_{24}H_{46}$	237°-240°	"	0.8639
C_nH_{2n-4}	$C_{23}H_{42}$	253°-255°	"	0.8842
"	$C_{24}H_{44}$	263°-265°	"	0.8864
"	$C_{25}H_{46}$	275°-278°	"	0.8912

II. THE HYDROCARBONS IN CANADIAN PETROLEUM WITH HIGH BOILING-POINTS.

BY CHARLES F. MABERY.

In a former paper¹ the constituents of Canadian Corniferous limestone petroleum distilling below 216° were described and were shown, by analysis and determination of molecular weights, to belong to the series C_nH_{2n+2} , to the hydrocarbon $C_{11}H_{22}$ boiling at 196°. The hydrocarbon boiling at 216° was found to be $C_{12}H_{24}$. Since several series have appeared in Pennsylvania and Ohio Trenton limestone crude oil, it seemed of interest to ascertain the series which form the main constituents of Canadian petroleum in the portions with high boiling-points. The distillates separated as a part of the former work were available for the study of the higher constituents.² Examination of the fraction collected at 216° was repeated and further results were obtained in verification of the former work which assigned the formula $C_{12}H_{24}$ to this hydrocarbon.

A determination of molecular weight established the formula $C_{12}H_{24}$.

0.4528 gram oil and 23.375 grams benzene gave a depression of 0.555.

¹ *Loc. cit.*² A part of this work was performed by Mr. E. T. Numsen, who selected it as the subject of a thesis for the degree of Bachelor of Science.

Calculated for
 $C_{12}H_{24}$
 168

Found.
 171

The chlorine product was formed by the action of chlorine on the hydrocarbon standing over water. On fractionating the product most of it collected at 160° (15 mm.) and this distillate gave sp. gr. 0.9145 at 20° .

The percentage of chlorine corresponded to the formula $C_{12}H_{23}Cl$.

0.1910 gram oil gave 0.1338 gram $AgCl$.

Calculated for
 $C_{12}H_{24}$
 17.52

Found.
 17.32

The molecular weight of the chlorine product, at the freezing-point of benzene, agreed with the value required by the same formula.

0.361 gram oil and 20.79 grams benzene gave a depression of $0^{\circ}.425$.

Calculated for
 $C_{12}H_{23}Cl$
 202.5

Found.
 200

Distillation of the higher fractions was repeated several times, to collect, so far as possible, the hydrocarbons within narrow limits.

Hydrocarbon $C_{13}H_{26}$, *B. P.* 228° – 230° .—The next fraction examined collected at 228° – 230° after the twentieth distillation. Without purification it gave sp. gr. 0.8087 at 20° . After thorough agitation with concentrated and fuming sulphuric acid the sp. gr. was 0.7979, which agrees closely with that of the hydrocarbon $C_{13}H_{26}$ separated from Ohio petroleum.

Analysis gave values required for the series C_nH_{2n} .

0.1614 gram oil gave 0.5068 gram CO_2 and 0.2060 gram H_2O .

	Calculated for $C_{13}H_{26}$	Found.
C	85.70	85.64
H	14.30	14.28

A determination of the molecular weight gave values required for $C_{13}H_{26}$.

0.4631 gram oil and 17.79 grams benzene gave a depression of $0^{\circ}.689$.

Calculated for $C_{13}H_{26}$.	Found.
182	185

This formula was further verified by determination of its index of refraction, 1.444, which corresponded to the molecular refraction :

Calculated for $C_{13}H_{26}$.	Found.
59.84	60.59

The formula was still further confirmed by its chloride, which was formed by passing chlorine through the purified oil, over water, in diffuse sunlight, until sufficient was absorbed to form the greatest yield of monochloride. After several distillations *in vacuo*, a considerable portion collected at 165° (15 mm.). A Carius determination gave a percentage of chlorine required for the monochloride.

0.1548 gram oil gave 0.1014 gram $AgCl$.

	Calculated for $C_{13}H_{25}Cl$.	Found.
Cl	16.40	16.20

The molecular weight of the chloride was determined by the freezing-point method.

0.3069 gram oil and 19.14 grams benzene gave a depression of $0^{\circ}.355$.

Calculated for $C_{13}H_{25}Cl$.	Found.
216.5	220.4

The formula was also shown by its index of refraction, 1.465, which corresponded to the molecular refraction :

Calculated for $C_{13}H_{25}Cl$.	Found.
64.78	65.02

The sp. gr. of the chloride found was 0.9221.

Hydrocarbon $C_{14}H_{28}$, B. P. 141° – 143° (50 mm.).—After the

twentieth distillation a fraction collected, in considerable quantity, within the limits 141° – 142° (50. mm.) and gave, without purification, sp. gr. 0.8206 at 20° . After purification with concentrated and fuming sulphuric acid its sp. gr. was 0.8099. This hydrocarbon was shown by analysis to be of the series C_nH_{2n} :

I. 0.1657 gram oil gave 0.5185 gram CO_2 and 0.2135 gram H_2O .

II. 0.1656 gram oil gave 0.5201 gram CO_2 and 0.2079 gram H_2O .

	Calculated for $C_{14}H_{28}$.	I.	Found. II.
C	85.70	85.34	85.65
H	14.30	14.35	14.04

The formula was shown by its molecular weight.

0.3121 gram oil and 18.46 grams benzene gave a depression of $0^{\circ}.418$.

Calculated for $C_{14}H_{28}$.	Found.
196	198

The hydrocarbon gave an index of refraction of 1.449, which corresponded to the molecular refraction of the same formula :

Calculated for $C_{14}H_{28}$.	Found.
64.44	65.02

The hydrocarbon distilled under atmospheric pressure, with some decomposition, at 244° – 248° . Further confirmation of the formula was obtained by the composition of the chloride, which was formed in the manner described above. The product of chlorination was fractionally distilled, which caused a considerable portion to collect at 180° (15 mm.) ; the sp. gr. of the chloride was 0.9288 at 20° . The percentage of chlorine agreed with that required for the monochloride.

0.1690 gram substance gave 0.1039 gram $AgCl$.

	Calculated for $C_{14}H_{27}Cl$.	Found.
Cl	15.40	15.21

The molecular weight was found at the freezing-point of benzene.

0.7890 gram substance and 23.80 grams benzene gave a depression $0^{\circ}.718$.

Calculated for $C_{14}H_{27}Cl$.	Found.
230.5	226.4

The index of refraction, 1.471, corresponded to the same molecular weight.

Calculated for $C_{14}H_{27}Cl$.	Found.
69.39	69.35

Another fraction of the chlorine product collected in considerable quantity at 197° – 200° (15 mm.); after purification, it boiled near to 200° and gave sp. gr. 1.0066 at 20° . The percentage of chlorine indicated a dichloride.

0.1669 gram substance gave 0.1680 gram AgCl.

	Calculated for $C_{14}H_{26}Cl_2$.	Found.
Cl	26.80	24.90

The low percentage of chlorine is doubtless due to incomplete chlorination. The index of refraction found, 1.489, corresponds to the molecular refraction of the dichloride.

Calculated for $C_{14}H_{26}Cl_2$.	Found.
74.33	76.12

Hydrocarbon $C_{15}H_{30}$, B. P. 159° – 160° (60 mm.).—As a considerable portion of the distillates collected constant at 159° – 160° (50 mm.), after the twentieth distillation, this fraction was selected for the identification of the next hydrocarbon, which proved to be $C_{15}H_{30}$. It gave sp. gr. 0.8311 at 20° , before purification and, after thorough agitation with concentrated and fuming sulphuric acid, 0.8192. Determinations of carbon and hydrogen indicate the series C_nH_{2n} .

0.1586 gram oil gave 0.4961 gram CO_2 and 0.2007 gram H_2O .

	Calculated for $C_{15}H_{30}$.	Found.
C	85.70	85.30
H	14.30	14.16

This formula was indicated by the molecular weight determined at the freezing-point of benzene.

0.3634 gram oil and 19.276 grams benzene gave a depression of $0^{\circ}.443$.

Calculated for	Found.
$C_{15}H_{30}$.	
210	208

This formula was confirmed by the molecular refraction, calculated from the index found, 1.452.

Calculated for	Found.
$C_{15}H_{30}$.	
69.04	69.15

A portion of the hydrocarbon was chlorinated and the product distilled until it came together in large amount at 190° (15 mm.) ; its sp. gr. was 0.9358 at 20° . Determinations of chlorine established its composition.

I. 0.1579 gram substance gave 0.0951 gram AgCl.

II. 0.2032 gram substance gave 0.1158 gram AgCl.

	Calculated for	I.	Found.	II.
	$C_{15}H_{29}Cl$.			
Cl	14.45	14.55		14.09

For further identification the molecular weight was ascertained.

0.4520 gram substance and 17.44 grams benzene gave a depression of $0^{\circ}.529$.

Calculated for	Found.
$C_{15}H_{29}Cl$.	
244.5	240

The index of refraction found, 1.455, corresponded to a molecular refraction of the same formula :

Calculated for	Found.
$C_{15}H_{29}Cl$.	
73.99	74.83

It would have been interesting to include in this examination the hydrocarbons with still higher boiling-points, to ascertain where the series C_nH_{2n-2} and C_nH_{2n-4} begin, for comparison with the corresponding distillates from other petroleum ; but the work described above exhausted the supply of dis-

tillates prepared from the large distillation of crude oil and the great amount of labor involved in working up to the well distilled fractions from the crude oil, prevented a repetition, on account of the attention demanded by more important lines of work.

The hydrocarbons described above, representing a considerable proportion of Canadian petroleum, correspond, in boiling-points and in composition, to those separated from Ohio Trenton limestone petroleum. An explanation of the higher specific gravity of Canadian crude oil and commercial products obtained from it, as compared with Ohio, Pennsylvania, West Virginia, Kentucky and similar crude oils, is given by the larger proportion, in the Canadian oil, of the series C_nH_{2n} and series poorer in hydrogen. In the Canadian crude oil this series begins in the fraction 196° , a temperature much lower than that at which it is found in any of the other petroleums mentioned and, no doubt, it forms a much larger proportion of the crude oil. The same is doubtless true of the series still poorer in hydrogen. As shown in a former paper, the series C_nH_{2n} does not appear in Pennsylvania petroleum until the hydrocarbon $C_{17}H_{34}$ is reached; but in Pennsylvania petroleum the first hydrocarbon of this series is $C_{11}H_{22}$. In Ohio petroleum the series begins with the hydrocarbon $C_{12}H_{24}$.

Doubtless the changes in series in the crude oil are more gradual than appears from our results. One distillation, as conducted in a refinery, affords only a partial separation, but in long-continued fractionations the tendency toward collection "in heaps" indicates an accumulation of the hydrocarbons in the vicinity of their boiling-points. The smaller quantities which collect between are composed of mixtures of higher and lower boiling hydrocarbons; doubtless the larger portion is not entirely free from higher and lower boiling constituents. Perhaps this causes a balancing of molecular weights, but it is evident that the contaminating higher and lower bodies are not sufficient in amounts to interfere with determinations that establish the formula of the principal hydrocarbon.

The following table gives the hydrocarbons separated from

Canadian petroleum and the chlorides prepared from them, with their boiling-point and specific gravity :

	Formula.	Boiling-point.		Sp. gr. at 20°.
Hydrocarbon	$C_{12}H_{24}$	216°		
Chloride	$C_{12}H_{23}Cl$	160°	15 mm.	0.9145
Hydrocarbon	$C_{13}H_{26}$	228°-230°		0.8087
Chloride	$C_{13}H_{25}Cl$	165°	" "	0.9221
Hydrocarbon	$C_{14}H_{28}$	141°-143°	50 "	0.8096
Chloride	$C_{14}H_{27}Cl$	180°	15 "	0.9288
Hydrocarbon	$C_{15}H_{30}$	159°-169°	50 "	0.8192
Chloride	$C_{15}H_{29}Cl$	190°	15 "	0.9358

III. HYDROCARBONS IN SANTA BARBARA CRUDE OIL.

Composition of California Petroleum (Continued).

In a paper¹ published two years ago, allusion was made to a specimen of peculiar heavy petroleum that had been received from Mr. J. B. Bardwell, Summerland, Santa Barbara County, Cal., representing the heavy oil that is taken from wells sunk below the Pacific Ocean. An examination of this petroleum seemed desirable, especially because it is the heaviest specimen, with one exception, that has been examined in this laboratory. It represents the last member of a series beginning with the light-yellow Berea Grit oil from Southern Ohio, which was found by Mabery and O. C. Dunn² to be the lightest petroleum that had come to our knowledge.

This work was undertaken by Mr. C. V. Zoul.³ The oil, as it was received, had the consistency of heavy tar ; it would scarcely flow at ordinary temperatures.

Its sp. gr. was 0.9845 at 20° ; it contained 0.84 per cent sulphur, 1.25 per cent nitrogen, 86.32 per cent carbon and 11.70 per cent hydrogen, showing that the crude oil is composed, at least to a large extent, of hydrocarbons poorer in hydrogen than petroleum from most other sources. In attempting to ascertain the composition of this petroleum, 2,000 grams were fractionated under 60 mm., collecting within 5°. The first distillate came over at 200° (atmospheric pressure) and only small amounts were collected below 175° (60 mm.). The distillation was car-

¹ P. Am. Acad., 36, 255.

² THIS JOURNAL, 18, 1 (1896).

³ The subject of a thesis for the degree of Bachelor of Science.

ried to 365° , without attempting to collect closer than in 5° fractions, because the principal object was to ascertain the form of the hydrocarbons, although, as will appear, the fractions gave fairly close values for their molecular weights.

The heavy character of the constituents of this petroleum is shown by the specific gravity of several distillates after the fifth distillation.

150° - 155° .	305° - 310° .	325° - 330° .	240° - 245° .
0.8649	0.9641	0.9739	0.9778

The residue at 365° from 2,000 grams was 200 grams, which showed that the greater portion of the oil distilled between 150° and 360° , or within a range of about 200° . Only 85 grams came over below 150° (60 mm.); at higher temperatures the fractions collected in larger amounts at certain points and these distillates were selected to ascertain the series of hydrocarbons :

	155° - 160° .	175° - 180° .	195° - 200° .	210° - 215° .
Weights	25	70	50	75
	223° - 230° .	250° - 255° .	310° - 315° .	340° - 345° .
Weights	75	50	80	45

Hydrocarbon $C_{18}H_{24}$, *B. P.* 150° - 155° (60 mm.).—Before treatment with acids, the distillate 150° - 155° gave sp. gr. 0.8649 at 20° and 0.8621 after purification with concentrated and fuming sulphuric acid and sodium hydroxide.

The percentages of carbon and hydrogen corresponded to the formula $C_{18}H_{24}$.

0.1357 gram oil gave 0.4312 gram CO_2 and 0.1653 gram H_2O .

	Calculated for $C_{18}H_{26}$.	Found.
C	86.67	86.68
H	13.33	13.62

The molecular weight of this hydrocarbon, at the freezing-point of benzene, indicated the same formula.

0.3641 gram oil and 18.17 grams benzene gave a depression of $0^{\circ}.541$.

Calculated for
 $C_{13}H_{24}$.
 180

Found.
 181.5

A determination of the index of refraction gave 1.4681, from which the molecular refraction was calculated :

Calculated for
 $C_{13}H_{24}$.
 57.74

Found.
 58.05

Hydrocarbon $C_{16}H_{30}$, *B. P.* 175° – 180° (60 mm.).—The fraction 175° – 180° was rather thick and viscous, with sp. gr. 0.8832 at 20° ; after purification it had practically the same, 0.8808. Percentages of carbon and hydrogen corresponded to the formula $C_{16}H_{30}$.

0.1533 gram oil gave 0.4879 gram CO_2 and 0.1797 gram H_2O .

Calculated for
 $C_{16}H_{30}$.
 C 86.48
 H 13.52

Found.
 86.82
 13.11

A determination of molecular weight, at the freezing-point of benzene, gave the same formula.

0.7134 gram oil and 16.56 grams benzene gave a depression of $0^{\circ}.974$.

Calculated for
 $C_{16}H_{30}$.
 222

Found.
 216.7

The index of refraction was found to be 1.470, which gave the molecular refraction for the formula $C_{16}H_{30}$.

Calculated for
 $C_{17}H_{30}$.
 71.6

Found.
 70.3

Hydrocarbon $C_{17}H_{30}$, *B. P.* 190° – 195° (60 mm.).—Very little difference in specific gravity of this distillate was found before and after purification. The values were 0.8969 and 0.8919, respectively. The proportions of carbon and hydrogen indicated a change in series from C_nH_{2n-2} in the preceding hydrocarbons to C_nH_{2n-4} .

0.1444 gram oil gave 0.4628 gram CO_2 and 0.1664 gram H_2O .

	Calculated for $C_{17}H_{30}$.	Found.
C	87.18	87.40
H	12.82	12.90

Determination of the molecular weight, at the freezing-point of benzene, gave a value for the formula $C_{17}H_{30}$.

0.8220 gram oil and 18.20 grams benzene gave a depression of $0^{\circ}.921$.

	Calculated for $C_{17}H_{30}$.	Found.
	234	240

The index of refraction was found to be 1.4778, corresponding to the molecular refraction :

	Calculated for $C_{17}H_{30}$.	Found.
	74.03	74.27

Hydrocarbon $C_{18}H_{32}$, *B. P.* 210° – 215° (60 mm.).—The viscous distillate 210° – 215° gave sp. gr. 0.9085; after thorough treatment with concentrated and fuming sulphuric acid in gasoline solution, the value was 0.8996. The carbon and hydrogen percentages agreed with the series C_nH_{2n-4} .

0.1494 gram oil gave 0.4787 gram CO_2 and 0.1713 gram H_2O .

	Calculated for $C_{18}H_{32}$.	Found.
C	87.10	87.38
H	12.90	12.83

An 18-carbon compound was shown by a determination of its molecular weight, at the freezing-point of benzene.

0.8281 gram oil and 18.94 grams benzene gave a depression of $0^{\circ}.864$.

	Calculated for $C_{18}H_{32}$.	Found.
	248	248

The index of refraction was found to be 1.484 at 20° and the molecular refraction :

	Calculated for $C_{18}H_{32}$.	Found.
	78.64	78.86

Hydrocarbon $C_{24}H_{44}$, *B. P.* 250° – 255° (60 mm.).—The viscous distillate 250° – 255° gave sp. gr. 0.9299 at 20° , and carbon and hydrogen percentages for the series C_nH_{2n-4} .

0.1481 gram oil gave 0.4745 gram CO_2 and 0.1628 gram H_2O .

	Calculated for $C_{24}H_{44}$.	Found.
C	87.42	87.40
H	12.58	12.29

Determinations of the molecular weight, at the freezing-point of naphthalene, gave results corresponding to the formula $C_{24}H_{44}$.

I. 0.5682 gram oil and 11.66 grams naphthalene gave a depression of $1^{\circ}.022$.

II. 0.4777 gram oil and 12.21 grams naphthalene gave a depression of $0^{\circ}.819$.

Calculated for $C_{24}H_{44}$.	I.	Found.	II.
332	329		330

Hydrocarbon $C_{27}H_{46}$, *B. P.* 310° – 315° (60 mm.).—This distillate was very thick and viscous. For purification it was dissolved in light gasoline; after treatment the gasoline was distilled in a current of carbon dioxide. The original distillate gave sp. gr. 0.9548, which, by treatment with acid, became 0.9451, with practically no change.

The carbon and hydrogen had values required for the series C_nH_{2n-8} .

I. 0.1479 gram oil gave 0.4757 gram CO_2 and 0.1588 gram H_2O .

II. 0.1486 gram oil gave 0.4769 gram CO_2 and 0.1613 gram H_2O .

	Calculated for $C_{27}H_{46}$.	I.	Found.	II.
C	87.59	87.72		87.52
H	12.41	12.00		12.13

A determination of its molecular weight, at the freezing-point of benzene, gave a value required for a 27-carbon compound.

0.3985 gram oil and 17.488 grams benzene gave a depression of $0^{\circ}.300$.

Calculated for $C_{27}H_{46}$.	Found.
370	372

This formula was supported by the index of refraction, 1.5146, from which the molecular refraction was calculated.

Calculated for

$C_{27}H_{46}$.

116

Found.

118

Hydrocarbon $C_{29}H_{50}$. B. P. 340° – 345° (60 mm.).—This distillate was purified as before in light gasoline. After the gasoline was removed there remained an extremely viscous, light-yellow oil, that would scarcely flow at ordinary temperatures; sp. gr. 0.9778 at 20° . The original fraction had scarcely any odor, consequently contained no phenol derivative.

The purified oil gave the following values for carbon and hydrogen:

0.1489 gram oil gave 0.4781 gram CO_2 and 0.1634 gram H_2O .

Calculated for

$C_{29}H_{50}$.

C

87.44

Found.

87.76

H

12.56

12.28

The higher distillates were not examined, because the results described above are sufficient to establish the composition of the main body of the crude oil. The difficulties in separating hydrocarbons at these high temperatures at all well-fractionated and of obtaining analytical values to decide their composition, are very great. It is evident that the series of hydrocarbons which compose Santa Barbara petroleum, explains the peculiar nature of the oil, which is unlike any other that has been examined in this laboratory. The most volatile distillates are composed of the series C_nH_{2n-2} , and the proportion of hydrogen gradually falls off through the series C_nH_{2n-4} and C_nH_{2n-6} . This change is accompanied by a corresponding increase in specific gravity. These viscous hydrocarbons evidently approach the constituents of the asphaltic oils and natural tars. It is easy to see how petroleum is converted, by slow evaporation under natural conditions, into the great beds of tars and asphalts and this affords the most probable explanation of their formation.

The hydrocarbons described in this paper, with their boiling-point and specific gravity, are brought together in the following table:

Hydrocarbons Separated from Santa Barbara (Cal.) Petroleum.

Hydrocarbon	Formula.	Boiling-point.	Sp. gr. at 20°.
"	$C_{13}H_{24}$	150°-155°, 60 mm.	0.8621
"	$C_{16}H_{30}$	175°-180°, "	0.8808
"	$C_{17}H_{30}$	190°-195°, "	0.8919
"	$C_{18}H_{32}$	210°-215°, "	0.8996
"	$C_{24}H_{44}$	250°-255°, "	0.9299
"	$C_{27}H_{46}$	310°-315°, "	0.9451
"	$C_{29}H_{50}$	340°-345°, "	0.9778

IV. SEPARATION OF SOLID PARAFFIN HYDROCARBONS FROM PETROLEUM WITHOUT DISTILLATION.

BY CHARLES F. MABERY AND OTTO J. SIEPLEIN.

By the method of distillation, which is the only means for the separation of the petroleum hydrocarbons, it is not possible to determine whether the solid paraffin hydrocarbons are contained in the crude oil or whether they may not be formed by decomposition.

As a direct proof that the solid hydrocarbons are actually contained in petroleum we have separated them without distillation. Three kilos of an average specimen of Pennsylvania crude petroleum were allowed to stand in a shallow pan, exposed to a current of air, in a strong flue draft, for thirty days. The change was shown by the increase in specific gravity :

Sp. gr. at 15° before exposure.		
Dec. 9.	Dec. 12.	Jan. 8.
0.815	0.840	0.862

When taken from the flue, January 8th, the residue weighed 1 kilo, which showed a loss of 66.67 per cent. The original oil distilled as follows :

50°-150°.	150°-200°.	200°-250°.	250°-300°.	+300°.
21 per cent	11 per cent	11 per cent	13 per cent	42 per cent

The residue above 300° is, therefore, about the same in weight as the residue left by evaporation. That the loss by evaporation had practically ceased at the end of one month was shown by allowing the residue to stand one year in the same place, exposed to draft as before, but there was no change in weight nor in specific gravity.

Combustion of the crude oil :

0.1968 gram oil gave 0.4915 gram CO_2 and 0.2512 gram H_2O .

C	85.51
H	14.18

Combustion of the residue after thirty days' evaporation :

0.1559 gram oil gave 0.4925 gram CO_2 and 0.1559 gram H_2O .

C	86.16
H	13.69

Evaporation of the portions with lower boiling-points, which form the greater part of the series $\text{C}_n\text{H}_{2n+2}$, leaves a larger proportion or series poorer in hydrogen, C_nH_{2n} and $\text{C}_n\text{H}_{2n-2}$, corresponding to the composition shown by analyses.

On cooling with ice the residue from evaporation became quite solid.

On distillation, 28 per cent came over below 30° , 6 per cent at 300° – 360° , with a residue above 360° of 66 per cent.

The amount of solid hydrocarbons in the residue was determined by the method suggested by Zaliziecki. Fifty grams of the residue with fused oil, mostly isoamyl alcohol, was allowed to stand at 0° for 24 hours; 250 grams alcohol were then added and the precipitate collected on a filter and washed with a mixture of fusel oil and alcohol. The precipitate on the filter-paper was then placed in an extraction apparatus and extracted with benzene. After evaporation of the benzene the residue was heated to 140° for 1 hour to remove the last traces of fusel oil. Nineteen and eight-tenths grams of a greenish-black solid remained, melting at 32° , equivalent to 39.6 per cent of the heavy residue, or to 14 per cent of the original oil, before evaporation.

The solid was again dissolved in fusel oil and precipitated by alcohol, giving a smaller quantity melting at 45° . This treatment, repeated, gave a light-brown substance melting at 57° , which was then dissolved in ether and precipitated by alcohol; this product had less color and another treatment gave a white solid melting at 61° . Its sp. gr. was 0.7966 at

70°, corresponding to that of paraffin and it gave percentages of carbon and hydrogen required for paraffin hydrocarbons.

0.1511 gram substance gave 0.4730 gram CO₂ and 0.1984 gram H₂O.

C	85.37
H	14.69

The specific gravity, melting-point and composition of this substance indicate that it was composed of paraffin hydrocarbons and demonstrated the presence of solid paraffin hydrocarbons in Pennsylvania petroleum.

Paraffin collected from heavy distillates in the refinery is, therefore, obtained as it exists in the original crude oil and is not formed during distillation. Indeed, as explained in another paper, it cannot be formed, for any decomposition of petroleum hydrocarbons by heat removes hydrogen, with a conversion of the hydrocarbon substances into a lower series; for example, of the paraffin hydrocarbons of the series C_nH_{2n+2} into the series C_nH_{2n} , C_nH_{2n-2} , etc. and, perhaps, also forming methylenes and condensed methylenes. Such changes do not involve an absorption of oxygen into the hydrocarbon molecule, but a removal of hydrogen, by oxygen, as water. That oxygen compounds of the nature of phenols are found in petroleum from various fields has been fully demonstrated independently by Richardson and by Mabery (data not published) and it is quite probable that most petroleum contains these bodies to a greater or less extent; but they have been formed by natural processes.

In ordinary refinery distillation there is probably little decomposition below 300°, but at this point "cracking" begins and increases rapidly to the end. There are, doubtless, reactions at higher temperatures between nitrogen, sulphur and oxygen compounds. Then the breaking down in series begins, with loss of hydrogen, through the asphaltic hydrocarbons, until finally coke is reached, which forms a considerable proportion of the products of refining.

V. THE SOLID PARAFFIN HYDROCARBONS THAT COLLECT IN CERTAIN OIL WELLS IN PENNSYLVANIA.

In attempting to determine the series of hydrocarbons and

members of the series that form the solid constituents of Pennsylvania petroleum, it seemed of interest to examine the semi-solid product that collects in considerable quantities in some of the Pennsylvania wells, especially at Coreopolis, Pa. The Petrolatum Co. collects large quantities of this pasty substance from their wells and from it manufactures various preparations, such as vaseline and cosmoline. The crude product is obtained in the form of a light-yellow, pasty mass, from which it is impossible to separate a solid by pressure in filter-paper or by filtration. It evidently consists of an emulsion of the high-boiling oils with the solid hydrocarbons, which, no doubt, are in part dissolved in the oily constituents.

Having obtained several gallons of this substance through the kindness of the Coreopolis Petrolatum Company in October, 1898, I undertook an examination of it with the principal object of proving the presence of solid hydrocarbons and identifying their composition, as to series and molecular formulas, for comparison with the solid hydrocarbons which I have separated from Pennsylvania crude oil and from commercial paraffin. These semi-solid emulsions have, no doubt, been formed by evaporation of the lighter constituents of petroleum and the solid hydrocarbons are, therefore, what were contained in the original petroleum. An opportunity was also afforded to confirm the presence of the solid constituents of paraffin in crude petroleum, a question concerning which a doubt is often expressed by refiners.

The specimen was received in the form of a thick paste, with sp. gr. 0.8345 at 60°. In beginning the distillation 9380 grams were distilled in a porcelain still, under 50 mm. pressure and the distillates collected in the following quantities :

	-195°.	195°-200°.	200°-245°.	245°-265°.	265°-285°.
Grams	905	865	895	850	830
	285°-315°.	315°-330°.	330°-342°.		Residue.
Grams	200	790	885		3000

Distillation of these fractions was continued within 10°, 5° and 2° until, after the sixth distillation, larger quantities collected at the following temperatures :

242°-244° 268°-270° 280°-282° 308°-310° 328°-330°
 340°-342° 352°-354° 368°-370° 382°-384°

Because the distillates below 268° showed, by their thin pasty condition, that they contained only small proportion of solid hydrocarbon, no attempts were made to separate their constituents. The fraction 272°-274° gave sp. gr. 0.8116 at 20° and the following percentages of carbon and hydrogen :

0.1600 gram substance gave 0.5058 gram CO₂ and 0.1963 gram H₂O.

Calculated for C ₂₅ H ₄₈ .	Found.
86.21	86.22
13.79	13.73

This fraction, therefore, consisted mainly of a hydrocarbon of the series C_nH_{2n-2}, and the same will appear in the higher fractions to be described.

On cooling the distillates with salt and ice and attempting to separate the solid by filtration under pressure, the emulsion was so complete that scarcely any of it remained on the filter ; but such a wide difference was observed in the solubility in ether and alcohol, between the crystalline and amorphous solid, that it afforded an easy means of separation.

The distillate 272°-274° (30 mm.) was, therefore, dissolved in a suitable mixture of ether and alcohol, cooled with salt and ice and filtered cold. The solid collected was pressed and the crystallization repeated, which gave a perfectly white crystalline hydrocarbon melting at 50°-51°, giving sp. gr. 0.7900 at 60° and carbon and hydrogen indicating the series C_nH_{2n+2}.

0.1516 gram substance gave 0.4728 gram CO₂ and 0.1973 gram H₂O.

	Calculated for tetracosane, C ₂₄ H ₅₀ .	Found.
C	85.21	85.06
H	14.79	14.56

The quantity of the solid hydrocarbon obtained was small, evidently not sufficient to influence the proportions of carbon and hydrogen in the unfiltered distillate. Although the amount obtained was not enough for a determination of its

molecular weight, its melting-point and specific gravity, identical with those of the hydrocarbon tetracosane separated from the paraffin distillate 272° – 274° , indicate that it has the same composition.

Tetracosane, obtained by Krafft¹ by reduction of the ketone derived from barium stearate and barium heptylate, melted at 51° , but the specific gravity of Krafft's hydrocarbon was somewhat lower than that of the hydrocarbon from petroleum.

The quantities of the distillates between 274° and 316° were too small to permit of a separation of crystalline hydrocarbons in sufficient amounts for identification of individual constituents.

The pasty solid collected at 316° – 318° (50 mm.) yielded a solid hydrocarbon, by crystallization from alcohol and ether, that melted at 66° . The crude distillate gave sp. gr. 0.8212 at 20° .

0.1564 gram substance gave 0.4935 gram CO_2 , and 0.1939 gram H_2O .

	Calculated for hentricontane, $\text{C}_{28}\text{H}_{54}$.	Found.
C	86.15	86.05
H	13.85	13.80

The purified solid gave sp. gr. 0.7997 at 70° and carbon and hydrogen required for the series $\text{C}_n\text{H}_{2n+2}$.

0.1499 gram substance gave 0.4698 gram CO_2 and 0.1969 gram H_2O .

	Calculated for $\text{C}_{31}\text{H}_{64}$.	Found.
C	85.31	85.45
H	14.69	14.69

The formula of this hydrocarbon was further verified by its molecular weight.

0.3648 gram substance and 12.12 grams naphthalene gave a depression of $0^{\circ}.471$.

	Calculated for $\text{C}_{31}\text{H}_{64}$.	Found.
	436	441

¹ Ber. d. chem. Ges., 15, 1718 (1882).

From the ketone palmiton, $C_{31}H_{62}O$, Krafft¹ prepared hentri-contane, $C_{31}H_{64}$, m. p. $68^{\circ}.1$, which differs but slightly from that of the hydrocarbon separated from petroleum, 66° .

Because the solid hydrocarbon formed such a small proportion of the original distillate that it did not affect materially the composition of the latter, it evidently could not be compared with the hydrocarbon separated from the corresponding distillate from paraffin, nor with that from crude Pennsylvania petroleum, for the predominating constituents should materially affect the boiling-points of all the minor solid ones. This is shown to be true by the high molecular weights and high melting-points of the hydrocarbons separated from Coreopolis distillates, so far as they could be determined. The distillate collected at 328° – 330° (50 mm.), after filtration from the solid, had sp. gr. 0.8235 at 70° ; after crystallization from ether and alcohol the white solid had sp. gr. 0.7982 at 70° . The proportions of carbon and hydrogen agreed with the formula of the series C_nH_{2n+2} .

The original distillate gave sp. gr. 0.8217. Analysis :

0.1586 gram substance gave 0.4995 gram CO_2 and 0.1925 gram H_2O .

	Calculated for $C_{29}H_{60}$.	Found.
C	86.14	85.86
H	13.86	13.57

The solid, purified by means of ether and alcohol, gave proportions of carbon and hydrogen corresponding to the series C_nH_{2n+2} .

0.1549 gram solid gave 0.4842 gram CO_2 and 0.2075 gram H_2O .

	Calculated for $C_{32}H_{66}$.	Found.
C	85.33	85.25
H	14.67	14.98

The melting-point of the crystalline hydrocarbon was 67° – 68° ; its molecular weight, at the boiling-point of benzene and also at the freezing-point of naphthalene, indicated the next higher homologue, $C_{32}H_{66}$, dotricontane, but the small quantity

¹ Ber. d. chem. Ges., 15, 1714.

of substance available for this determination was not sufficient to yield satisfactory results.

The specific gravity of the unpurified distillate 342° – 344° (50 mm.) was 0.8288; after separation of the solid by freezing and purification by crystallization from ether and alcohol, its sp. gr. was 0.8005 at 75° and it melted at 68° – 70° . The unpurified distillate gave carbon and hydrogen corresponding to the series C_nH_{2n-2} .

0.1517 gram substance gave 0.4784 gram CO_2 and 0.1850 gram H_2O .

	Calculated for $C_{30}H_{58}$.	Found.
C	86.12	86.06
H	13.88	13.64

The purified solid gave proportions of carbon and hydrogen required for the series C_nH_{2n+2} .

0.1544 gram solid gave 0.4816 gram CO_2 and 0.2060 gram H_2O .

	Calculated for $C_{32}H_{66}$.	Found.
C	85.33	85.06
H	14.67	14.92

The molecular weight, determined by the boiling-point method, confirmed the formula $C_{32}H_{66}$.

0.5127 gram substance and 12.23 grams benzene gave a depression of $0^{\circ}.654$.

	Calculated for $C_{32}H_{66}$.	Found.
	438	442

As mentioned above, the solid hydrocarbons form a small proportion of the original oil; the small amounts that collect at 328° – 330° and 340° – 342° have, doubtless, nearly the same composition, $C_{32}H_{66}$.

The distillate 366° – 368° (50 mm.), before treatment, had sp. gr. 0.8312; the solid hydrocarbon separated by freezing, filtration and crystallization from ether and alcohol, had sp. gr. 0.8009 at 80° and melted at 71° – 72° . The carbon and hydrogen in the unpurified distillate corresponded to the formula C_nH_{2n-2} .

0.1485 gram substance gave 0.4982 gram CO_2 and 0.1851 gram H_2O .

	Calculated for $\text{C}_{81}\text{H}_{60}$.	Found.
C	86.11	85.96
H	13.89	13.94

The solid separated from the fraction $366^\circ\text{--}368^\circ$, after purification, gave 85.41 per cent carbon and 14.74 per cent hydrogen, corresponding to the series $\text{C}_n\text{H}_{2n+2}$; it was present in only small quantity and probably differed but slightly from the hydrocarbon contained in the fraction $342^\circ\text{--}344^\circ$.

The close agreement to the series $\text{C}_n\text{H}_{2n-2}$, in the composition of the untreated distillate, before removing the solid hydrocarbon, is due, as explained above, to the very small proportion of the latter, which is $\text{C}_n\text{H}_{2n+2}$. The oils separated by filtration are evidently composed, for the greater part, of the series $\text{C}_n\text{H}_{2n-2}$, although the low percentage of hydrogen may indicate the presence, in small amounts, of a series even poorer in hydrogen.

The untreated distillate $380^\circ\text{--}384^\circ$ (50 mm.) gave sp. gr. 0.8336, and the solid hydrocarbon obtained by freezing, filtration and crystallization from ether and alcohol, 0.8052 at 80° . It melted at 76° . Determinations of carbon and hydrogen indicated the series $\text{C}_n\text{H}_{2n-2}$.

0.1560 gram substance gave 0.4898 gram CO_2 and 0.1943 gram H_2O .

	Calculated for $\text{C}_{34}\text{H}_{26}$.	Found.
C	86.08	95.82
H	13.92	13.93

The purified solid contained carbon and hydrogen required for the series $\text{C}_n\text{H}_{2n+2}$.

0.1501 gram solid gave 0.4695 gram CO_2 and 0.1974 gram H_2O .

	Calculated for $\text{C}_{85}\text{H}_{72}$.	Found.
C	85.37	85.33
H	14.63	14.71

The molecular weight of the solid, by the boiling-point method, corresponded to the same formula.

1.0012 gram substance and 24.72 grams benzene gave a rise of $0^{\circ}.212$.

Calculated for $C_{35}H_{72}$.	Found.
492	490

As the molecular weights of the hydrocarbons of these series increase, the determinations become more and more difficult and uncertain. The values obtained, together with the other data, support the formulas given. With the high-boiling liquids there is less trouble than with solids.

As formerly explained, the freezing-point of benzene cannot be relied on for solid hydrocarbons with molecular weights much above $C_{20}H_{42}$. At its boiling-point, benzene can be depended on for a somewhat higher range, but becomes uncertain with hydrocarbons in the vicinity of $C_{30}H_{62}$. Other solvents are equally uncertain on account of a lack of solubility or variable influence of the dissolved substance on the freezing-point. After long trial with naphthalene, which promised reliable results on account of its free solvent power and large depression, we found that the substances which had melting-points not far removed from that of naphthalene gave variations in depression too great for reliable calculations of molecular weights.

Solid Hydrocarbons in Pennsylvania Oil Wells.

	Formula.	Melting-point.	Specific gravity.
Tetracosane	$C_{24}H_{50}$	$50^{\circ}-51^{\circ}$	0.7900 at 60°
Hentricontane	$C_{31}H_{64}$	66°	0.7997 at 70°
Dotricontane	$C_{32}H_{66}$	$67^{\circ}-68^{\circ}$	0.8005 at 75°
Tetratricontane	$C_{34}H_{70}$	$71^{\circ}-72^{\circ}$	0.8009 at 80°
Pentatricontane	$C_{35}H_{72}$	76°	0.8052 at 80°

Hydrocarbons of the series C_nH_{2n+2} have now been identified in Pennsylvania petroleum in continuous series, with but few members wanting, from butane, C_4H_{10} , b. p. -10° , to pentatricontane, $C_{35}H_{72}$, b. p. $380^{\circ}-384^{\circ}$, 50 mm.

VI. COMPOSITION OF COMMERCIAL PARAFFIN.¹

It has been questionable, even with refiners of petroleum of

¹ A part of the work described in this paper was performed by Mr. H. R. Payne, and formed the subject of a thesis for the degree of Bachelor of Science.

all esters p. 647.

long experience, as to whether paraffin is actually present in the crude oil or whether it is a result of change during the process of refining. It therefore seemed of interest to ascertain whether the hydrocarbons, of which commercial paraffin is composed, are identical with the solid constituents of the crude oils that yield paraffin.

The method of distillation was the same as that employed in distilling the crude oil, except that it was found necessary to pack the neck of the flask with a thick coating of asbestos. With exclusion of air it was found that paraffin could be distilled definitely with no decomposition, but introduction of air, either by leaks or by accident, caused serious decomposition, as shown by the dark color and disagreeable odor of the distillates.

Fifteen hundred grams of the best commercial paraffin was distilled under 40 mm. and the distillates collected at first within 10°, then 5° and finally within 2°, altogether seven times. The lowest distillate collected below 250° and the final residue, above 350°, was only 30 grams. All the distillates were colorless, except the residue, which was slightly brown and nearly odorless. The distillates collected in larger quantities at temperatures corresponding to the boiling-points of hydrocarbons separated from the crude oil as follows :

	Grams.		Grams.
256°-258°	90	316°-318°	35
272°-274°	45	332°-334°	20
282°-284°	70	346°-348°	40
292°-294°	30		

Tricosane $C_{23}H_{48}$, *B. P.* 256°-258° (40 mm.).—The distillate 256°-258°, without purification, melted at 48° and this was not raised by crystallization from alcohol and ether. *Tricosane* obtained by Krafft¹ melted at 47°.7. Its sp. gr. was determined above its melting-point :

60°	0.7836	70°	0.7814	80°	0.7807
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The sp. gr. of tricosane from petroleum differs materially from that of the hydrocarbon which Krafft obtained from the ketone, laurone :

¹ Ber. d. chem. Ges., 15, 1713 (1882).

47°.7 0.7785 80°.8 0.7570 88°.8 0.7456

Carbon and hydrogen were in proportions required for the series C_nH_{2n+2} .

0.1510 gram substance gave 0.4710 gram CO_2 and 0.1989 gram H_2O .

	Calculated for $C_{23}H_{48}$.	Found.
C	85.20	85.06
H	14.80	14.73

A determination of its molecular weight, at the boiling-point of benzene, gave a value required for tricosane.

0.8907 gram solid and 24.24 grams benzene gave a rise of 0°.295.

Calculated for $C_{23}H_{48}$.	Found.
324	319

Tetracosane $C_{24}H_{50}$, *B. P.* 272°–274° (40 mm.).—This distillate melted, without purification, at 50°–51° and was not changed by crystallization from alcohol and ether. Krafft's tetracosane, obtained from the ketone derived from barium stearate and barium heptylate, melted at 51°.1. The quantity of tetracosane obtained was not sufficient to determine its specific gravity.

This hydrocarbon was shown, by analysis, to belong to the series C_nH_{2n+2} :

I. 0.1424 gram substance gave 0.4451 gram CO_2 and 0.1923 gram H_2O .

II. 0.1460 gram substance gave 0.4551 gram CO_2 and 0.1955 gram H_2O .

III. 0.1443 gram substance gave 0.4502 gram CO_2 and 0.1924 gram H_2O .

	Calculated for $C_{24}H_{50}$.	I.	Found. II.	III.
C	85.21	85.25	85.00	85.08
H	14.79	14.96	14.97	14.91

The formula was verified by a determination of its molecular weight.

3.0316 gram oil and 22.42 grams benzene gave a rise of 1°.034.

Calculated for
 $C_{24}H_{50}$.

338

Found.

335

Pentacosane $C_{25}H_{52}$, *B. P.* 282° – 284° (40 mm.).—The melting-point of the unpurified distillate, 282° – 284° , was 53° – 54° ; after crystallization from ether and alcohol it melted at 54° . Its sp. gr. was determined above its melting-point.

60°	0.7911	80°	0.7870
70°	0.7881	90°	0.7854

Analysis:

0.1467 gram substance gave 0.4578 gram CO_2 and 0.1950 gram H_2O .

Calculated for
 $C_{25}H_{52}$.

Found.

C	85.23	85.09
H	14.77	14.88

The formula was confirmed by a determination of its molecular weight.

1.4324 grams substance and 8.5282 grams benzene gave a rise of $1^{\circ}.265$.

Calculated for
 $C_{25}H_{52}$.

352

Found.

354

Hexacosane $C_{26}H_{54}$, *B. P.* 294° – 296° (40 mm.).—After the seventh distillation, 25 grams, collected at 294° – 296° , melted at 55° – 56° and was not changed by crystallization from ether and alcohol. Its sp. gr. above its melting-point was :

60°	0.7938	80°	0.7893
70°	0.7918	90°	0.7879

The carbon and hydrogen corresponded to the series C_nH_{2n+2} .

0.1526 gram solid gave 0.4757 gram CO_2 and 0.2027 gram H_2O .

Calculated for
 $C_{26}H_{54}$.

Found.

C	85.23	85.02
H	14.77	14.86

Its molecular weight, found at the boiling-point of benzene, verified the formula.

1.6742 grams substance and 13.151 grams benzene gave a rise of $0^{\circ}.93$.

Calculated for $C_{26}H_{54}$.	Found.
366	365

Octocosane $C_{28}H_{58}$, *B. P.* 316° – 318° (40 mm.).—At 316° – 318° 35 grams collected after the seventh distillation with m. p. 60° which was not changed by crystallization from ether and alcohol. The carbon and hydrogen indicated the series C_nH_{2n+2} .

0.1586 gram oil gave 0.4954 gram CO_2 and 0.2122 gram H_2O .

	Calculated for $C_{28}H_{58}$.	Found.
C	85.28	85.17
H	14.72	14.96

A determination of its molecular weight corresponded to the formula $C_{28}H_{58}$.

I. 1.3337 grams solid and 23.73 grams benzene gave a rise of $0^{\circ}.362$.

II. 1.7964 grams solid and 21.96 grams benzene gave a rise of $0^{\circ}.53$.

Calculated for $C_{28}H_{58}$.	I.	Found.	II.
394	397		396

Nonocosane $C_{29}H_{60}$, *B. P.* 346° – 348° (40 mm.).—At 346° – 348° 40 grams collected, m. p. 62° – 63° . It gave percentages of carbon and hydrogen indicating the series C_nH_{2n+2} .

0.1520 gram solid gave 0.4752 gram CO_2 and 0.2062 gram H_2O .

	Calculated for $C_{29}H_{60}$.	Found.
C	85.28	85.27
H	14.72	14.87

Molecular weight determinations :

I. 1.6181 gram substance and 23.57 grams benzene gave a rise of $0^{\circ}.41$.

II. 1.6236 grams substance and 23.99 grams benzene gave a rise of $0^{\circ}.402$.

Calculated for $C_{29}H_{60}$.	I.	Found.	II.
406	405		408

The solid distilling above 350° has the composition of the series C_nH_{2n+2} as shown by analysis :

0.1469 gram solid gave 0.4581 gram CO_2 and 0.1947 gram H_2O .

	Calculated for $C_{30}H_{62}$.	Found.
C	84.31	85.04
H	14.69	14.82

Because only 2 per cent of the original paraffin taken for distillation remained as a residue at 350° , the solid hydrocarbons composing the main body of paraffin produced in the refinery are evidently members of the series C_nH_{2n+2} . They do not contain oxygen, as is frequently stated, at least not those that can be distilled. It is not reasonable to assume that they have been formed from other constituents by "cracking," because such decompositions give rise to hydrocarbons of lower molecular weight. It is well known that paraffin, when exposed to air, may be decomposed completely by heat into lower hydrocarbons. In mass we have found that it may be distilled indefinitely by exclusion of air, but it cannot be distilled in air without decomposition.

Thorpe and Young¹ subjected shale paraffin to distillation, under pressure, in a bent tube so arranged that the paraffin could be repeatedly distilled. The distillation was continued until the solid was converted into bodies that remained liquid at ordinary temperatures. This liquid proved to consist of two series of hydrocarbons ; of the series C_nH_{2n+2} , the hydrocarbons C_5H_{12} to $C_{11}H_{24}$ were identified and of the series C_nH_{2n} the ethylene hydrocarbon compounds C_5H_{10} to $C_{11}H_{22}$.

It is our intention to examine the products of the distillation of paraffin in air to observe the changes in "cracking". It is an interesting question as to whether any relation exists between the paraffin hydrocarbons and the methylenes, with reference to the organic origin of these bodies and whether the series are interconvertible by natural agencies.

¹ Ber. d. chem. Ges., 5, 556 (1872).

Hydrocarbons in Commercial Paraffin.

	Formula.	Melting-points.	Specific gravity.
Tricosane	$C_{23}H_{48}$	48°	0.7886 at 60°
Tetracosane	$C_{24}H_{50}$	50°-51°	
Pentacosane	$C_{25}H_{52}$	53°-54°	0.7941 at 60°
Hexacosane	$C_{26}H_{54}$	55°-56°	0.7968 at 60°
Octocosane	$C_{28}H_{58}$	60°	
Nonocosane	$C_{29}H_{60}$	62°-63°	

VII. COMPOSITION OF COMMERCIAL VASELINE, COSMOLINE, AND SIMILAR PRODUCTS.

After ascertaining the composition of the constituents of Pennsylvania petroleum with high boiling-points and the composition of the semi-solid product used at Coreopolis for the manufacture of the medicinal preparations, it seemed of interest to investigate the composition of the commercial products for comparison with specimens obtained directly from the wells. On account of the very high boiling-points, it is only possible to distil *in vacuo*. Under 15 mm., 100 grams of vaseline (Ceroleum) distilled in the following proportions:

	-250°.	250°-275°.	275°-300°.	300°-325°.	325°-350°.	350°-360°.	Residue.
Grams	14	22	14	18	7	20	6

The distillates were light-yellow and, when melted, showed a slight fluorescence. Below 250° the distillate was a heavy, viscous liquid, the others all semi-solid and the residue was brown. To ascertain whether solids could be separated from these distillates, the fraction 250°-275° was dissolved in ether and sufficient alcohol added to precipitate the solid hydrocarbon. The solid was again dissolved in ether and precipitated by alcohol. After filtration it had no greasy feel and melted at 70°. From the fraction 350°-360°, after similar treatment, a solid was obtained which melted at 77°-78°. These substances resembled in all respects the solid paraffin hydrocarbons. It is, therefore, evident that vaseline is composed of heavy oils such as have been identified as forming the portions of Pennsylvania petroleum with high boiling-points, and Coreopolis heavy oil, hydrocarbons of the series C_nH_{2n} , C_nH_{2n-2} and C_nH_{2n-4} , together with solid paraffin hydrocar-

bons. The quantity of solid paraffins is sufficient to saturate the oil and, in slight excess, to form an emulsion of the desired consistency.

What is known as "scale" paraffin in the refineries is composed of solid hydrocarbons, with enough of the heavy oils to form a greasy solid. But the solid constituents are hydrocarbons of the same series, C_nH_{2n+2} , which cannot be changed into other forms without decomposition. These hydrocarbons are only sparingly soluble in the liquid hydrocarbons of lower boiling-points of the same series, but they dissolve more freely in the series with high boiling-points, C_nH_{2n+2} , C_nH_{2n} , C_nH_{2n-2} and C_nH_{2n-4} .

Since the work described in these papers was begun ten years ago, I have received efficient aid from the following assistants: in distillation, Messrs. C. Lindmueller, D. H. Walker, C. R. Cummins, and H. A. Triebing; in distillation and analysis, Mr. C. S. Richards; analysis and molecular weight determinations, Mr. O. J. Sieplein.

It is my intention to make later a summarization, in a separate communication, of the results published from the beginning in this series of papers on petroleum.

Contributions from the Chemical Laboratory of Harvard College.

ON 4-NITRO-5-PYRAZOLONE.¹

BY H. B. HILL AND O. F. BLACK.

During an investigation of the oximes of nitromalonic aldehyde, W. J. Hale and one of us² made the observation that, when nitromalonic diacetyldialdoxime,

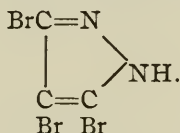


was dissolved in a hot solution of sodic hydrate, the sodium salt of a new acid was formed, which was shown, by the analysis of its silver salt, to be an isomer of fulminuric acid, $C_3H_3N_3O_3$. The results of the further study of this substance are contained in the following paper.

¹ Most of the work described in this paper was done under the direction of Professor Hill, but it was finished and the paper written after his lamented death. C. L. J.

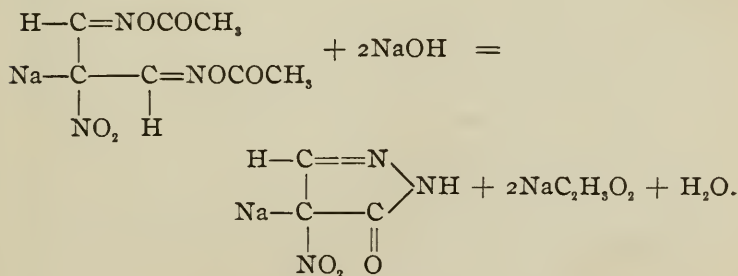
² THIS JOURNAL, 29, 253 (1903).

The substance, $C_3H_3N_3O_3$, melted at $136^\circ-137^\circ$ and formed well-defined salts, of which the sodium salt, $NaC_3H_2N_3O_3 \cdot 3H_2O$, the silver salt, $AgC_3H_2N_3O_3$, the barium salt, $Ba(C_3H_2N_3O_3)_2 \cdot 4H_2O$ and the lead salt, $Pb(C_3H_2N_3O_3)_2$, were analyzed. By the action of a stream of air, loaded with bromine vapor, on the aqueous solution of the sodium salt a new compound, $C_3HN_2Br_3$, was obtained, which was remarkably stable, as it sublimed unaltered and was not decomposed by long boiling with sodic hydrate in strong aqueous solution nor even with an alcoholic solution. These properties indicated a ring-shaped structure for the molecule and in that case the formula would show that the substance is tribromopyrazol,



Its observed properties agree with this theory of its constitution, as it dissolves even in weak solutions of the alkalies and is precipitated unaltered by acids; it forms an unusually stable silver salt and with sodium amalgam it gives a purple color.

The bromine derivative being established as a substituted pyrazol, it was probable that the sodium salt, $NaC_3H_2N_3O_3$, from which it was made, also had a ring structure and would probably be the 4-nitro-5-pyrazolone, which could be formed from the nitromalonic diacetyldialdoxime by the following reaction:



To test this theory we tried the action of phosphoric oxy-

chloride on our sodium salt, since Michaelis and Röhmer¹ have shown that this reagent converts many pyrazolones into the corresponding chlorpyrazol; upon heating the substances together, in a sealed tube, at 100°, we obtained 4-nitro-5-chlorpyrazol, agreeing, in melting-point and properties, with that made by Oskar Meder² by the action of nitric acid on 5-chlorpyrazol. Meder gives the melting-point 185°–188°; we found 186°–187°. There can be no doubt, therefore, that our salt is the sodic 4-nitro-5-pyrazolone and this theory is confirmed by its properties, especially by the fact that it turns purple when treated with sodium amalgam.

A secondary product of the preparation of the tribrompyrazol was obtained in too small quantity for thorough study. A single determination of bromine indicated that it might be a dibromnitypyrazol.

EXPERIMENTAL PART.

Preparation of Sodic Nitromalonic Diacetyldialdoxime.—This substance³ was prepared as follows: Six grams of the hydrochlorate of hydroxylamine, dissolved in 20 cc. of 5N sodic hydrate, were mixed with 6 grams of the sodium salt of nitromalonic aldehyde, dissolved in 20 cc. of water and the mixture allowed to stand until crystals of the sodic dialdoxime began to appear. Twenty cc. of 5N sodic hydrate were then added, the liquid diluted with about one-half its volume of water and poured into eight test-tubes, which were kept cooled by immersion in ice-water. Small quantities of acetic anhydride were added to each test-tube in turn and the contents shaken until the mixture became nearly solid from the formation of the light-yellow, finely-crystalline precipitate of the diacetyl body, which was then washed with cold water, filtered on the pump and dried on a porous plate. The yield of sodic nitromalonic diacetyldialdoxime averaged 9 grams.

Sodic 4-Nitro-5-pyrazolone, $\text{NaC}_3\text{H}_2\text{N}_3\text{O}_3$.—To prepare this compound 2.53 grams of the dry sodic nitromalonic diacetyl-

¹ Ber. d. chem. Ges., **31**, 2908 (1898).

² Inaug. Diss., Jena, 1901. We cannot find that this work has been published in any journal.

³ Hill and Hale: THIS JOURNAL, **29**, 264 (1903).

dialdoxime were added to 20 cc. of sodic hydrate, previously warmed in a porcelain dish on the water-bath; these weights give 2 molecules of sodic hydrate for each molecule of the diacetyl body. The bright red solution thus obtained, after evaporation to about one-half its volume on the steam-bath, yielded, on cooling, a mass of fine orange-yellow needles of the new salt. This, however, could not be purified conveniently for analysis by recrystallization from water, as it was very hard to remove, in this way, a small impurity of sodic acetate, which has about the same solubility in water as the new substance. The specimens for analysis were therefore prepared by neutralizing, with pure sodic hydrate, the pure acid made in the manner described later in this paper:

0.3276 gram salt, dried on filter-paper, lost 0.0573 gram when exposed to the air.

	Calculated for $\text{NaC}_3\text{H}_2\text{N}_3\text{O}_3\cdot 3\text{H}_2\text{O}$.	Found.
$2\text{H}_2\text{O}$	17.56	17.50

0.1972 gram air-dried salt lost 0.0203 gram at 120° .

	Calculated for $\text{NaC}_3\text{H}_2\text{N}_3\text{O}_3\cdot \text{H}_2\text{O}$.	Found.
H_2O	10.65	10.30

From these analyses it appears that the salt contains 3 molecules of water, two of which are given off on exposure to the air. The third molecule was removed by heat, but not by drying over sulphuric acid.

I. 0.1998 gram salt, dried *in vacuo* over sulphuric acid, gave 0.0844 gram Na_2SO_4 .

II. 0.1769 gram salt, dried at 120° , gave 0.0834 gram Na_2SO_4 .

	Calculated for $\text{NaC}_3\text{H}_3\text{N}_2\text{O}_3\cdot \text{H}_2\text{O}$. $\text{NaC}_3\text{H}_2\text{N}_3\text{O}_3$.		Found.	
			I.	II.
Na	13.61	15.23	13.69	15.29

It crystallizes, by spontaneous evaporation from water, in dark-red prisms, which effloresce in the air, losing finally 2 molecules of water. It is soluble in water and sparingly soluble in alcohol. When treated with sodium amalgam, the reduced product turns purple on exposure to air.

4-Nitro-5-pyrazolone.—This substance was made by adding hydrochloric acid to a solution of the sodium salt in water and extracting with ether. On the addition of ligroin to the ethereal solution the body was deposited in small, colorless crystals, which melt at 136° – 137° . It is soluble in water, alcohol, or ether, less soluble in benzol, chloroform, or ligroin. It was not analyzed, but, as the specimens of the sodium salt which were analyzed were made from it, there can be no doubt about its composition.

Argentio 4-Nitro-5-pyrazolone, $\text{AgC}_3\text{H}_2\text{N}_3\text{O}_3$.—This salt was made by adding argentic nitrate either to the sodium salt or to the free pyrazolone. The precipitate from the sodium salt was washed with water and dried *in vacuo* for analysis.

I. 0.2229 gram substance gave 0.1774 gram AgBr.

II. 0.2358 gram substance gave 37.6 cc. N_2 at $22^{\circ}.3$ and 759.5 mm.

	Calculated for $\text{AgC}_3\text{H}_2\text{N}_3\text{O}_3$	I.	Found.
Ag	45.74	45.7 ^I	
N	17.79	. .	17.84

The salt forms a reddish-yellow powder, insoluble in cold or hot water.

Baric 4-Nitro-5-pyrazolone, $\text{Ba}(\text{C}_3\text{H}_2\text{N}_3\text{O}_3)_2 \cdot 4\text{H}_2\text{O}$.—This was made direct from the sodic nitromalonic diacetyldialdoxime by heating on the steam-bath an aqueous solution of that substance and baric hydrate, in the proportion of one molecule of each. The barium salt crystallized from the dark-red solution and was purified by recrystallization from hot water and dried on filter-paper for analysis.

1.0767 grams salt lost 0.1682 gram at 120° .

	Calculated for $\text{BaC}_6\text{H}_4\text{N}_6\text{O}_{14}\text{H}_2\text{O}$	Found.
H_2O	15.47	15.63

0.2365 gram salt, dried at 120° , gave 0.1402 gram BaSO_4 .

	Calculated for $\text{BaC}_6\text{H}_4\text{N}_6\text{O}_6$	Found.
Ba	34.93	34.89

It crystallizes in dark-red, efflorescent needles and is somewhat less soluble in water than the sodium salt, but otherwise resembles it closely.

Plumbic 4-Nitro-5-pyrazolone, $\text{Pb}(\text{C}_3\text{H}_2\text{N}_3\text{O}_3)_2$.—This salt was obtained, as a yellow precipitate, by adding a solution of plumbic acetate to one of the sodium salt. It was washed with cold water and dried *in vacuo* for analysis.

0.2655 gram salt gave 0.1741 gram PbSO_4 .

	Calculated for $\text{PbC}_6\text{H}_4\text{N}_6\text{O}_6$.	Found.
Pb	44.71	44.78

It forms a yellow powder only slightly soluble in hot water and nearly insoluble in the cold.

An acetylpyrazolone was made by shaking a solution of the sodium salt and sodic hydrate with acetic anhydride when the new compound was deposited as a white crystalline precipitate. After crystallization from a mixture of chloroform and ligroin it formed small, colorless prisms melting at 129° . Boiling with sodic hydrate converts it into the sodium salt again. It was not analyzed.

4-Nitro-5-chlorpyrazol, $\text{C}_3\text{H}_2\text{N}_3\text{ClO}_2$.—This substance was prepared from the 4-nitro-5-pyrazolone by heating it to 100° , in a sealed tube, with excess of phosphoric oxychloride. As the tube cooled the pyrazol crystallized out in needles, which were washed with cold water, recrystallized once from hot water and dried *in vacuo* for analysis.

0.2017 gram substance gave, by the Carius method, 0.2002 gram AgCl .

	Calculated for $\text{C}_3\text{H}_2\text{N}_3\text{ClO}_2$.	Found.
Cl	24.07	24.57

It forms fine white¹ needles, which melt at 186° – 187° . It is freely soluble in alcohol or acetone; slightly soluble in ether chloroform; slightly soluble in cold or freely soluble in hot water. These properties agree with those given by Oskar Meder (Inaug. Diss., Jena, 1901) for this substance, which he

¹ The compound, prepared as described, had a yellowish color, which was removed by treatment with bone-black.

prepared in a different way. His melting-point was 185° – 188° .

Tribromopyrazol, $C_3HN_2Br_3$.—When a stream of air, loaded with the vapor of bromine, was passed through a solution of the sodic 4-nitro-5-pyrazolone, a white flocculent precipitate was gradually formed, which consisted principally of tribromopyrazol, but, as it also contained a yellow gummy impurity, it is better to prepare the tribromopyrazol as follows: The sodic 4-nitro-5-pyrazolone, dissolved in a few cubic centimeters of strong hydrobromic acid, was mixed with an excess of bromine and heated in a sealed tube, to 100° , for two or three hours; in this way a good yield of fine, white needles was obtained. It was purified by washing with cold water and distillation with steam, dried *in vacuo* and analyzed:

I. 0.2158 gram substance gave 0.0920 gram CO_2 and 0.0140 gram H_2O .

II. 0.2863 gram substance gave 0.1240 gram CO_2 and 0.0140 gram H_2O .

III. 0.2351 gram substance gave 19.1 cc. N_2 at 24° and 762 mm.

IV. 0.1614 gram substance gave, by the Carius method, 0.2985 gram AgBr.

	Calculated for $C_3HN_2Br_3$.	I.	II.	Found. III.	IV.
C	11.79	11.63	11.81	. .	. .
H	0.31	0.74	0.54	. .	. .
N	9.18	. .	. .	9.13	. .
Br	78.65	. .	. .	. .	78.69

Properties of Tribromopyrazol.—It forms silky, white needles, which collect in matted masses looking like cotton. It melts at 181° , but sublimes at 120° or perhaps at a somewhat higher temperature. It distils with steam and is soluble in alcohol or ether; sparingly soluble in hot water, essentially insoluble in cold. It dissolves in sodic hydrate solution and is precipitated on the addition of an acid. When treated with sodium amalgam, the reduced product takes on a characteristic purple color on exposure to the air.

Argentio Tribromopyrazol, $AgC_3N_2Br_3$.—This salt was made by adding argentic nitrate, dissolved in water, to a solution of

tribrompyrazol in dilute alcohol, when a finely crystalline precipitate was formed which was washed with water and dried at 100° for analysis. The yield was quantitative. All our attempts to analyze it by the method of Carius failed, because we found it impossible to decompose it completely with nitric acid; we accordingly resorted to the electrolysis of the salt dissolved in potassic cyanide.

0.3246 gram salt gave 0.0843 gram Ag.

	Calculated for $\text{AgC}_3\text{N}_2\text{Br}_3$.	Found.
Ag	26.21	25.97

The salt forms a white crystalline powder, insoluble in hot water. It is slightly soluble in hot, strong nitric acid, but separates from the solution almost completely on cooling. It is a very stable substance, as it is not decomposed completely even when heated to 300° , with fuming nitric acid.

The acetyltribrompyrazol was made by dissolving tribrompyrazol in a solution of sodic hydrate and shaking the cooled mixture with acetic anhydride. It crystallizes from hot alcohol in white, felted needles, melting at 105° – 106° . Boiling with water converts it again into tribrompyrazol. It was not analyzed.

Secondary Product Formed in Making Tribrompyrazol.—

When the tribrompyrazol was prepared by the action of bromine vapor on sodic 4-nitro-5-pyrazolone, another substance was formed in small amount. This was obtained by concentrating the mother-liquors from the tribrompyrazol to a small volume. On cooling, the new compound separated in white crystals, which, however, were very impure. It was found that the best way to purify it consisted in further treatment with bromine, which formed an orange crystalline addition-compound; by boiling this with water, bromine was given off and the original white body was left in a state of purity. It was dried *in vacuo* for analysis.

0.1632 gram substance gave, by the Carius method, 0.2277 gram AgBr.

	Calculated for $\text{C}_3\text{HBr}_2\text{N}_3\text{O}_2$.	Found.
Br	59.03	59.35

The result of this analysis agrees very well with the percentage of bromine in a dibromnitropyrazol, but it is obvious that more analytical work is needed before this formula can be considered established. It crystallizes in white needles, melts at 163° - 164° and forms an acet compound, when treated with acetic anhydride and sodic hydrate.

Some of the bromine addition-product, made by the action of bromine on the substance just described, was washed with cold water, dried rapidly by pressing on filter-paper and analyzed.

0.1778 gram substance gave, by the Carius method, 0.2839 gram AgBr.

	Found.
Br	67.93

This result agrees excellently with that calculated for the addition of 1 molecule of bromine to 2 molecules of the dibromnitropyrazol; $C_6H_2Br_6N_6O_4$ contains 68.37 per cent of bromine. The analysis, however, is not entitled to much consideration, unless confirmed by additional work, as the substance loses bromine when exposed to the air and also by boiling with water, so that, even during the washing with cold water, some bromine might have been lost and there was certainly danger of such a loss during the drying and weighing. The addition-compound forms hard, orange crystals, insoluble in cold water, but decomposed by boiling with water with evolution of bromine and the formation of the white substance melting at 163° - 164° . We regret that we were unable to complete the investigation of these substances.

CAMBRIDGE, November 26, 1904.

Contributions from the Chemical Laboratory of Harvard College.

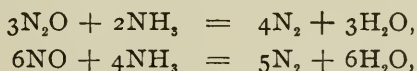
PURE NITROGEN FROM NITROUS AND NITRIC OXIDES AND AMMONIA.

BY GREGORY PAUL BAXTER AND CHARLES HENDEE HICKEY.

The preparation of nitrogen from ammonium nitrite necessitates subsequent purification from oxygen and oxygen compounds, by passing it over hot copper and offers many prac-

tical difficulties in the production of a regular and continuous current of gas. Nitrogen made from the air, by removing the oxygen with hot copper, with or without the addition of ammonia, contains about 1 per cent of argon, besides, of course, traces of the other inert gases. Hence a method of preparing nitrogen, at will, in large quantities, free from other gases, is likely to be of practical use. Such a method is described below.

Both nitrous and nitric oxides, when mixed with ammonia and ignited, combine with the latter gas to form nitrogen and water. In the case of nitrous oxide this combination takes place with almost the violence of an oxyhydrogen explosion.¹ In the case of nitric oxide, on the other hand, combination is complete only when the mixture is heated to a high temperature in the presence of a catalytic agent. Although, according to the equations



the volume of nitrogen which may be obtained from a given volume of nitrous oxide is almost double that which can be obtained from the same volume of nitric oxide, the ease with which nitric oxide may be prepared more than counterbalances the comparatively small yield of nitrogen. Hence the reaction with nitric oxide was investigated first.

The apparatus used in the experiments was as follows: A regular stream of nitric oxide was generated by dropping nitric acid, specific gravity about 1.2, upon copper turnings. This gas was conducted through a gas washing-bottle, containing strong ammonia, into a hard glass tube which contained two four-inch rolls of copper gauze, to act as the catalyzer. The tube was heated by a combustion furnace. The copper rolls remained perfectly bright during the experiment, indicating that ammonia was in excess and the gas which resulted, when collected over water, so that the excess of ammonia was ab-

¹ Dammer states that mixtures of ammonia and nitrous oxide explode when either ignited or sparked and that mixtures of ammonia and nitric oxide explode only when sparked, while at lower temperatures nitrogen, nitrogen oxides and water are produced. *Handb. d. anorg. Chem.*, II., 1, 34, 38.

sorbed, gave no evidence of nitric oxide by its odor. In order, however, to make certain of the purity of the nitrogen, the gas was subjected to the following test: It was first conducted through a solution of dilute sulphuric acid to remove the greater part of the ammonia; then through one Emmerling tower, containing fused stick potassium hydroxide, and two towers with glass pearls moistened with concentrated (freshly boiled) sulphuric acid, to remove moisture and the last traces of ammonia; after the gas had removed every trace of air, a small hard-glass tube, containing a roll of bright copper gauze, was connected with the last sulphuric acid column. The air in this tube was swept out and the copper heated with a full Bunsen flame. As no visible change in the appearance of the copper gauze had taken place at the end of one hour, it was evident that no nitric oxide remained in the nitrogen.

The well-known catalytic power of finely divided platinum led to a repetition of the above experiment, with platinized asbestos instead of copper. In one case, where poorly platinized asbestos was employed, some nitric oxide remained unattacked. A second attempt, with 2 inches of thoroughly platinized asbestos, resulted as successfully as in the case of copper.

Experiments were then carried out to determine the minimum concentration of ammonia solution in which the tension of ammonia was sufficiently large to yield, to the nitric oxide, an excess of ammonia over that necessary for the reaction. It was found that the nitric oxide was not completely acted upon if the specific gravity of the ammonia was above 0.925. Of course the minimum concentration of ammonia varies somewhat with temperature, with the rate at which the nitric oxide passes through the solution and with the form of the bottle containing it.

The use of copper, in the preparation of nitric oxide, makes the method somewhat expensive. Iron turnings mixed with a few small pieces of platinum were found to serve equally well. Small quantities of nitrous oxide or nitric peroxide, as impurity in the nitric oxide, could do no harm.

The following precautions are the most important in the successful production of pure nitrogen by this method.

1. The temperature of the catalytic agent must not be too low. Experiments where kerosene stoves were employed with the copper rolls showed only partial combination of the gases.

2. The ammonia should not be allowed to fall below the concentration corresponding to the sp. gr. 0.92.

3. If absolutely pure nitrogen is desired the materials must be purified. The metal used for the production of nitric oxide must be free from grease, the ammonia must be separated from amines and the purifying solutions must be boiled to expel air. The apparatus must be constructed entirely of glass, to avoid the introduction of sulphur and organic matter from the rubber.

Finally, a method was sought by which the explosion of the mixture of nitrous oxide and ammonia could be avoided. Nitrous oxide, when heated to a high temperature, decomposes into nitrogen and oxygen,¹ which do not explode when ignited with ammonia. The following apparatus was used for effecting this decomposition and for removing the oxygen by means of ammonia :

Nitrous oxide, produced by heating ammonic nitrate, was conducted through a short, hard glass tube in which a 2-inch section of platinized asbestos was heated to dull redness. The gases then passed through a wash-bottle containing concentrated ammonia solution. As the mixture showed no tendency to explode when ignited, it was considered safe to effect the reaction by conducting it through a second hard-glass tube, also containing a section of heated platinized asbestos. Complete combustion of the oxygen took place, for, when the resulting gas was freed from ammonia and water, as described above, a bright copper roll heated in it for some time remained unchanged.

The precautions to be observed in the use of the nitrous oxide are essentially the same as those mentioned in the case of nitric oxide. The platinized asbestos should be heated to as high a temperature as the hard-glass tubes will allow. "Blowing out" of the tubes may be prevented by wrapping the heated section in asbestos paper, to distribute the heat. The ammonia must not be too dilute, but more dilute ammo-

¹ Dammer : Handb. d. anorg. Chem., II., 1, 34.

nia may be employed here than in the case of nitric oxide, on account of the increase in volume when nitrous oxide is decomposed into nitrogen and oxygen.

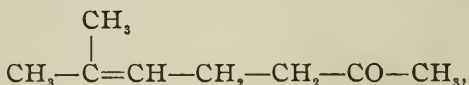
CAMBRIDGE, MASS.,
Dec. 2, 1904.

REPORT.

The Grignard Reaction.

Since the discovery of the compounds of zinc with organic radicals by Frankland¹, these substances have been of great assistance in organic synthesis, the similar sodium and mercury derivatives being of secondary importance. This is not the place to give an account of the difficulties met with in preparing and using these compounds, but so many investigators have entered the field opened by Grignard, that it is evident there was room for improvement in the old method.

Barbier² allowed methylheptenone,



to act on methyl iodide, in the presence of magnesium and obtained the tertiary alcohol, dimethyl-2,6-heptene-2-ol-6. This was surprising, for the zinc alkyls do not yield tertiary alcohols when they react with ketones and the method of Saytzeff, which was employed, is not applicable to ketones with the grouping $-\text{CO}-\text{CH}_3$.

Grignard³ undertook a general study of this and similar reactions. He soon found that magnesium is much more reactive than zinc and can be employed in many cases where the latter metal is useless. At first an attempt was made to isolate the organo-magnesium compounds, but this was soon abandoned. The work of Löhr,⁴ Fleck⁵ and of Waga⁶ showed that they are solids which are extremely unstable and act on alcohol and water with violence. They take fire in the air, or even in dry carbon dioxide and the only neutral solvent that can be used is a mixture of benzene and ether. The solution does not lend itself readily to reactions, besides which, the com-

¹ Ann. Chem. (Liebig), 85, 329 (1853). Phil. Trans., 142, 417 (1852).

² Compt. rend., 123, 110.

³ Ann. Chim. Phys., [7], 24, 433 (1901).

⁴ Ann. Chem. (Liebig), 261, 72.

⁵ Ibid., 276, 129.

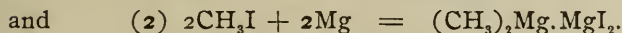
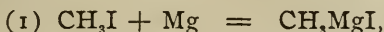
⁶ Ibid., 282, 320.

pounds could not be made conveniently, except by heating the alkyl iodides, in sealed tubes, with magnesium amalgam.

Frankland¹ and Wanklyn² had obtained substances such as $\text{Zn}(\text{C}_2\text{H}_5)_2 \cdot \text{O}(\text{C}_2\text{H}_5)_2$, etc., by heating zinc, an alkyl iodide and anhydrous ether, in sealed tubes. These compounds acted like the corresponding zinc alkyls. The reaction was, however, very incomplete and the reaction-product had to be distilled, as in the ordinary procedure, to effect a separation from the large solid mass that was formed.

With magnesium, which is much more strongly electropositive than zinc, we should expect the reaction to be more nearly complete and this was found to be the case. At the ordinary temperature, magnesium attacks methyl iodide, the reaction is complete and the product is soluble in ether. The method of work is comparatively simple. A mixture of the organic halide and anhydrous ether is allowed to drop slowly upon the calculated amount (1 molecule) of magnesium turnings, contained in a flask, provided with a return-condenser. Action begins at once and it is necessary to moderate it by cooling the flask. When all the magnesium has been dissolved, it is found that almost exactly 1 molecule of the halide has been used for each molecule of the metal. After warming a short time on the water-bath, the reaction-product is a nearly colorless liquid, containing a little dark powder, originating from traces of iron. Grignard found that the reaction took place with methyl, isopropyl, tertiary butyl and secondary hexyl iodides, with ethyl, propyl, isobutyl, isoamyl and benzyl bromides, as well as with brombenzene and bromnaphthalene. The ethereal solution thus obtained reacts violently with water, forming magnesium hydroxide and it is changed by moist air. Carbon dioxide acts upon it, giving a crystalline deposit. It acts energetically upon aldehydes, ketones and with the chlorides and anhydrides of acids. As the vapor of ether fills the apparatus, it is not necessary to work in an atmosphere of an inert gas. This is a great advantage over the zinc compounds.

There are two possible reactions between the organic halide and magnesium :



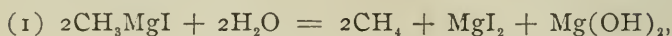
If the reaction is according to (2) the product cannot be $(\text{CH}_3)_2\text{Mg} + \text{MgI}_2$, for it has been shown that magnesium methyl is practically insoluble in ether³ and magnesium iodide

¹ Phil. Trans., 149, 412 (1859).

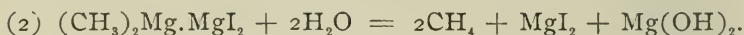
² J. Chem. Soc. (London), 13, 125 (1861).

³ Löhr: Ann. Chem. (Liebig), 261, 72. Fleck: *Ibid.*, 276, 129.

is also. Whether (1) or (2) is correct, we should obtain, in each case, 1 molecule of a saturated hydrocarbon for each molecule of halide, when water is allowed to act upon the product, thus :



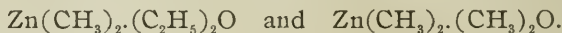
or



Experiment showed that methane was obtained in almost the theoretical amount.

When the ether was driven off by heating on the water-bath, an extremely viscous, dark gray mass remained. It contained some ether and its appearance was not changed even after heating for two days at 50° (10–12 mm.). It was then heated at 80° for three days, with frequent shaking, to renew the surface. Under these conditions the thinner parts, on the walls of the flask, became dry and had a light-brown tint, but the main portion consisted of a gum that could not be removed without breaking the flask. The dried substance changed rapidly in the air, becoming warm and reacted very violently with water. The methyl iodide compound was found to have the composition $\text{CH}_3\text{MgI} + \frac{2}{3}(\text{C}_2\text{H}_5)_2\text{O}$, and the ethyl bromide derivative was $\text{C}_2\text{H}_5\text{MgBr} + 28$ grams $(\text{C}_2\text{H}_5)_2\text{O}$. To remove the last traces of ether it was necessary to heat at 150° , in a vacuum, for several days. In this state the compounds were insoluble in anhydrous ether and seemed to be identical with those described by Löhr.¹

The tenacity with which they retain ether seems to show that it is held in much the same way as water of crystallization. Frankland² obtained the analogous derivatives,



The formation of these compounds is not unimportant, for, in the presence of benzene, ligroin, or other neutral solvent, the halogen compounds do not attack magnesium. On the other hand, the reaction goes very well in the presence of the different oxygen ethers, such as anisol and methyl isoamyl ether. Besides, the molecule of ether of crystallization makes the compounds soluble. It does not, however, enter into the reaction when the compounds are treated with ketones, etc.

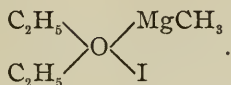
According to Schmidt³ these substances are derivatives of

¹ *Loc. cit.*

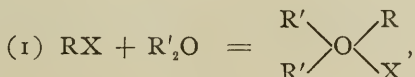
² *Phil. Trans.*, **149**, 412 (1859).

³ "Die basische Eigenschaften des Sauerstoffs und Kohlenstoffs," p. 17.

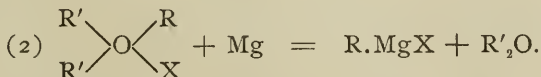
tetravalent oxygen, or, in other words, they are oxonium compounds. For example :



In a recent paper¹, Tschelinzeff gives his reasons for thinking that the ether simply plays the part of a catalytic agent. He found that the reaction takes place in the presence of very small quantities of ether, or anisol and, in some cases, even that may be dispensed with when bromides or iodides are used. Further, by working at a comparatively high temperature, a few halides yield the corresponding organo-magnesium compounds when neither ether nor benzene is present. Hence the reaction is typically catalytic, the ether simply favoring the dissociation of the halide and thus enabling the reaction to proceed more easily and at a lower temperature. He expresses it thus :



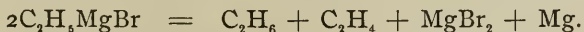
and



In an earlier paper² he showed that dimethylaniline or some other tertiary amine could be used in place of the ether and in this was confirmed by F. and L. Sachs,³ who used quinoline. Tschelinzeff found that $\text{R}'_2\text{N} \begin{array}{c} \text{R} \\ \diagdown \\ \text{X} \end{array}$ is formed, analogous to $\text{R}'_2\text{O} \begin{array}{c} \text{R} \\ \diagdown \\ \text{X} \end{array}$ and

the reaction goes so smoothly that he recommends the use of dimethylaniline, or other tertiary amine, in place of ether. The mixture is warmed until the reaction begins, or the liquid boils. At times a small crystal of iodine is used to start the action.

Grignard found that the compounds decompose with violence when heated to 250° or higher :



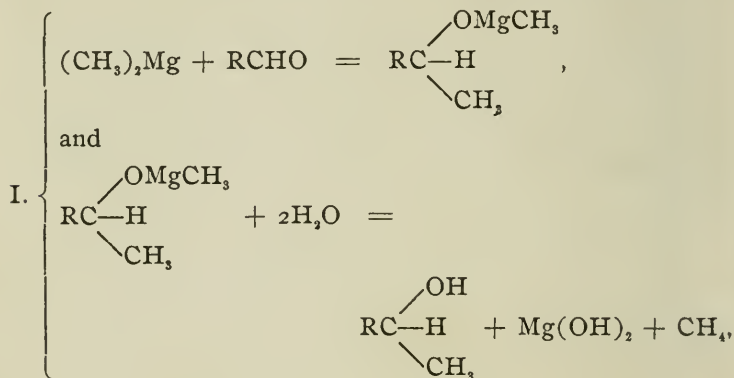
¹ Ber. d. chem. Ges., **37**, 4524 (1904).

² *Ibid.*, **37**, 2081 (1904).

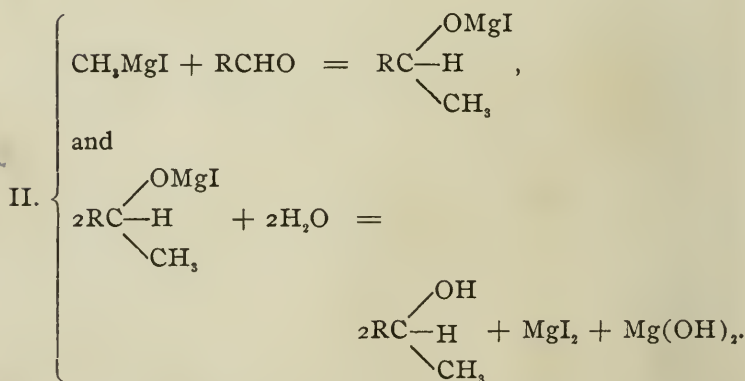
³ *Ibid.*, **37**, 3089 (1904).

The reaction does not proceed as smoothly as the equation indicates; the magnesium set free is at once oxidized by the traces of air in the flask.

Because the organo-magnesium halides are soluble in ether, react with water and acids without incandescence and do not take fire in the air, it is certain that they do not contain the grouping $\text{Mg}(\text{CH}_3)_2$ or $\text{Mg}(\text{C}_2\text{H}_5)_2$. If, to the product from one molecule each of magnesium and halide, we add one molecule of an aldehyde, there is obtained 0.6–0.8 molecule of a secondary alcohol. The reactions may take place as follows:



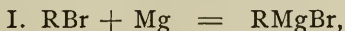
or



According to (I) there should be an evolution of gas when water is added. "In the second case the compound that is formed contains all the halogen that was introduced; in the first case, on the contrary, it does not contain a trace, for it

seems very probable that, if the grouping MgI_2 existed in the organo-magnesium compound it would be precipitated on combining with the aldehyde or ketone" (Grignard). Further, each molecule of halide should yield 0.5 molecule of alcohol, according to (I). As a matter of fact, no gas is ever evolved on adding water, the compounds are soluble in ether, or homogeneously crystalline (apparently without separation of magnesium iodide) and the yield is from 0.6–0.8 molecule of alcohol. Hence it seems most probable that the actual course of the reaction is as represented by (II.).

A secondary reaction takes place when magnesium is acted upon by the halogen derivative of a hydrocarbon. To a certain extent the metal acts like sodium in Wurtz's reaction, causing the formation of higher hydrocarbons, the amount of which depends on the number of carbon atoms in the halide. With isobutyl bromide the quantity of diisobutyl is usually too small to be purified; with isoamyl bromide the yield of diisoamyl is 10–15 per cent; with benzyl bromide the amount of hydrocarbon is 30–35 per cent, while with hexyl iodide there is formed about 50 per cent of dihexyl. Comparing the two reactions,



we see that, according to I, each molecule of halide requires one atom of magnesium, while if the reaction takes place as shown by II, only 0.5 atom of magnesium is needed for each molecule of halide. Grignard tried to suppress the secondary reaction as much as possible by using finer magnesium turnings, but no great difference was noticed in the results. It is useless to try to increase the exposed surface of metal by using magnesium powder, for it is always too much oxidized. Secondary halides showed a greater tendency to yield higher hydrocarbons than the corresponding primary ones and this was still more pronounced in the case of the tertiary halides. Tertiary butyl iodide gave a large amount of hydrocarbon, while nearly half of the magnesium was unchanged. Other methods for the preparation of hydrocarbons will be given later.

Löhr,¹ Fleck² and Waga³ stated that the symmetrical organo-magnesium compounds take fire in carbon dioxide. Grignard found that the gas also acts on the symmetrical compounds, but not violently, so that the reaction could be studied. If a current of the gas is passed into an ethereal solution of magne-

¹ Ann. Chem. (Liebig), 261, 72.

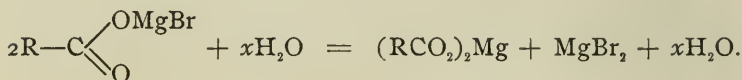
² Ibid., 276, 129.

³ Ibid., 282, 320.

sium methyl iodide, a crystalline deposit is at once formed. The reaction-mixture is poured upon crushed ice, acidified with dilute sulphuric acid and extracted with ether. The product is acetic acid. Isovaleric acid was made from isobutyl bromide. The following equations express the changes :



and



Similar reactions take place with organo-sodium compounds, but they are of greater theoretical interest than practical importance.¹

Numerous other chemists have used this reaction since it was first applied by Grignard. Zelinsky² found that hydroaromatic and cyclic hydrocarbons yield acids according to the reactions given above. He recommends, as an interesting lecture experiment,³ the preparation of benzoic acid from phenyl iodide. Schroeter⁴ found that, when phenyl bromide is used, the chief products are triphenylcarbinol, benzophenone, a little benzoic acid and a new compound which he did not identify. Houben and Kesselkaul⁵ and Bodroux also prepared acids by means of the reaction. The last author started with dihalogen derivatives of the aromatic hydrocarbons and found that only one of the halogen atoms reacts.⁶ From the monobromine derivatives of anisol and β -methoxynaphthalene he obtained the acids in which bromine is replaced by carboxyl.⁷ Houben and Kesselkaul found that carbon disulphide can be used in place of carbon dioxide.⁸ Among other acids they prepared phenyldithioacetic acid, $\text{C}_6\text{H}_5\text{CH}_2\text{CS}_2\text{H}$.

With carbonyl chloride⁹ tertiary alcohols are obtained, according to the equations :

¹ Wanklyn : Ann. Chem. (Liebig), 107, 125 ; 111, 234. Kekulé : *Ibid.*, 137, 180. R. Meyer u. Müller : Ber. d. chem. Ges., 15, 496, 698, 1905. Wanklyn and Schenk : Ann. Chem. (Liebig), Suppl., 6, 120.

² Ber. d. chem. Ges., 35, 2687.

³ *Ibid.*, 35, 2692.

⁴ *Ibid.*, 36, 3005.

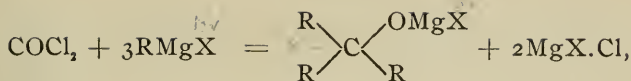
⁵ *Ibid.*, 35, 2519.

⁶ Bull. Soc. Chim., [3], 31, 24 (1904).

⁷ *Ibid.*, [3], 31, 30 (1904).

⁸ Ber. d. chem. Ges., 35, 3695.

⁹ Sachs u. Loewy : Ber. d. chem. Ges., 36, 1588 (1903). Grignard : Compt. rend., 136, 815 (1903).



and



Other reactions may also take place simultaneously, giving rise to ketones and secondary alcohols, as well as to unsaturated alcohols formed from them by loss of water.¹

Thiophosgene, CSCl_2 , also reacts readily with organo-magnesium halides.²

As in his principal article³ Grignard gives a general review of the subject up to that time, it will be followed closely in the remainder of this report, for much of the later work is but a development along lines laid down by him, or describes syntheses which he failed to carry out.

Before going further it may be well to give, in detail, the general method of work as described by Grignard. After the solution of the organo-magnesium compound has been prepared as stated (p. 305) the balloon flask containing it is cooled with water and the required amount of aldehyde, ketone, etc., dissolved in anhydrous ether, is allowed to drop into it slowly. A return-condenser is attached to the flask, for the reaction is quite energetic at first, each drop producing a hissing noise. The solid that separates sometimes dissolves, but may remain as a crystalline or viscous layer at the bottom. When all of the reagent has been added the contents of the flask are kept boiling gently on the water-bath, or, if too viscous, allowed to stand several hours at the ordinary temperature. The mixture is then slowly poured upon crushed ice and the magnesium hydroxide dissolved by adding small portions of hydrochloric or acetic acid. Theoretically, it is necessary to add only 1 molecule of acid, but a little more is always needed to make the liquid slightly acid. The ethereal layer is then decanted; if the product which is formed, for instance an alcohol, is soluble in water, the aqueous layer is distilled with steam and the alcohol separated from the distillate by means of potassium carbonate. The ethereal layer is washed with dilute sodium bicarbonate, to avoid the precipitation of magnesium, then with sodium acid sulphite to remove any aldehyde or ketone

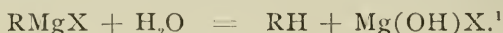
¹ Grignard: *Loc. cit.*

² Sachs u. Loevy: *Loc. cit.*

³ Ann. Chim. Phys., [7], 24, 433 (1901).

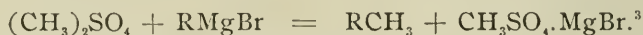
that may remain. The ether is then driven off, with suitable precautions and the residue is distilled or otherwise purified, according to its nature. Small amounts of polymerization-products are usually formed.

When treated with water, the organo-magnesium halides yield saturated hydrocarbons according to the equation :

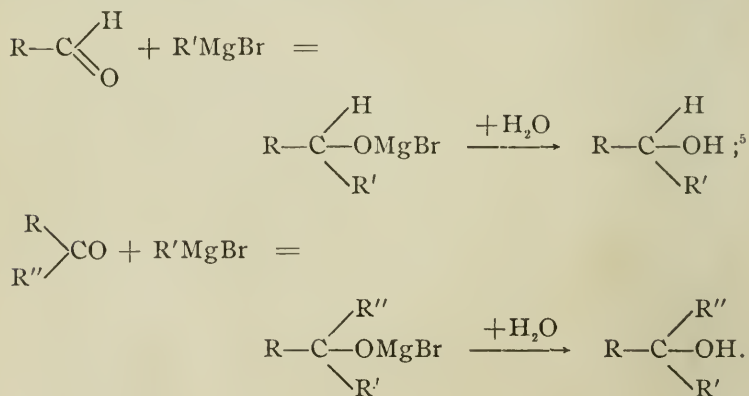


This reaction has been suggested as a means of detecting the hydroxyl group.²

Another way to make saturated hydrocarbons is by the reaction :



Aldehydes and ketones yield secondary and tertiary alcohols, respectively,⁴ as shown by the equations :



By analogous reactions phenols can be made.⁶ Thiophenols and selenophenols are prepared by the action of sulphur and selenium,⁷ respectively, on organo-magnesium compounds. The corresponding disulphides and diselenides are formed at the same time. These reactions led to a study of the action of

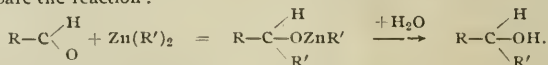
¹ Grignard : *Loc. cit.*

² Tschugaeff : *Ber. d. chem. Ges.*, **35**, 3912.

³ Werner u. Zilkens : *Ibid.*, **36**, 2116. Houben : *Ibid.*, **36**, 3083; **37**, 488. Werner : *Ibid.*, **36**, 3618.

⁴ Grignard : *Compt. rend.*, **130**, 1322. For other references see the bibliography.

⁵ Compare the reaction :

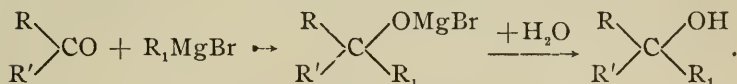


⁶ Bodroux : *Compt. rend.*, **136**, 158.

⁷ Taboury : *Bull. Soc. Chim.*, [3], **29**, 761; **31**, 581, 646, 1183.

oxygen on the organo-magnesium halides¹ and it was found that primary alcohols and phenols could be made in this way. Theoretically, the simplest method for the preparation of primary alcohols is by means of formic aldehyde and this has been accomplished by the action of its polymer, trioxymethylene, on the magnesium compound.²

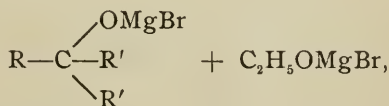
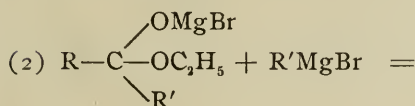
It is interesting to compare the reactions with the different classes of oxygen compounds. The aldehydes have already been mentioned. The ketones react in much the same way:³



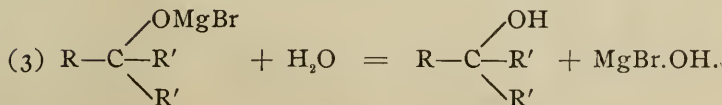
Diketones⁴ yield the corresponding pinacones.

The cyclic ketones⁵ react normally, as, in general, do other derivatives of the group.

The esters of mono- and dibasic aliphatic and aromatic acids react as shown by the equations:⁶



and



With the esters of ketone acids, either the ketone group acts alone or the carbonyl and carboxyl groups act simultaneously.⁷

¹ Bouveault : *Ibid.*, [3], 29, 1951 (1903).

² Grignard et Tissier : *Compt. rend.*, 134, 107 (1902).

³ Grignard : *Ann. Chim. Phys.*, [7], 24, 433 (1901).

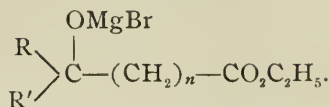
⁴ Zelinsky : *Ber. d. chem. Ges.*, 35, 2138 (1902).

⁵ Zelinsky u. Gutt : *Ibid.*, 35, 2140 (1902).

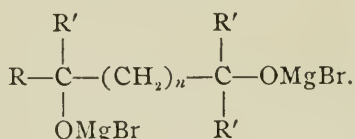
⁶ Grignard : *Compt. rend.*, 132, 136. Masson : *Ibid.*, 132, 483. Béhal, Tiffeneau et Sommelet : *Ibid.*, 132, 480. Valeur : *Ibid.*, 132, 833.

⁷ Grignard : *Ann. Chim. Phys.*, [7], 27, 548 (1902).

In no case was a compound formed by the action of the carbonyl group alone. We first obtain



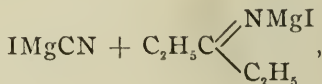
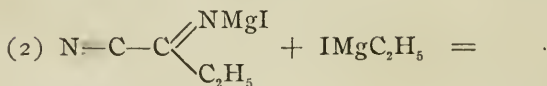
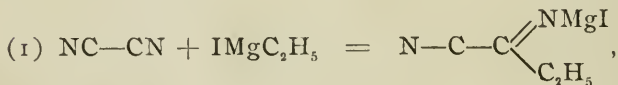
If this be treated with water the ester of an alcohol acid is formed; in some cases it at once combines with more of the magnesium organic halide, giving



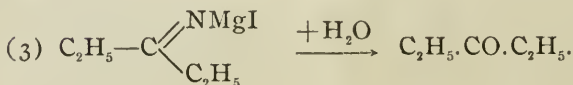
This yields a bitertiary glycol when treated with water.

Unsaturated hydrocarbons are frequently formed in working with compounds containing a large number of carbon atoms, on account of the loss of water by the alcohols which are originally produced. This was first noticed by Grignard and was made use of by other investigators.¹

Ketones can be made by the action of cyanogen or nitriles upon the organo-magnesium halides.²



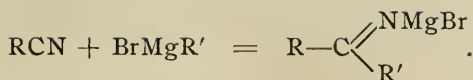
and



Similarly :

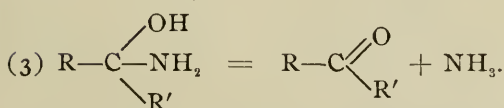
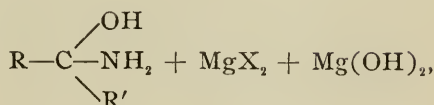
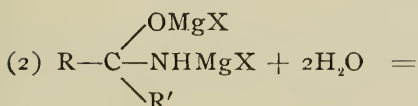
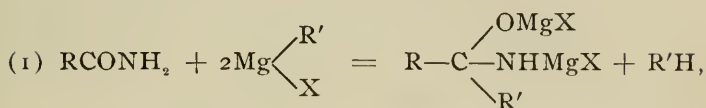
¹ Ann. Chim. Phys., [7], **24**, 433 (1901). Houben, Hell and Bauer, Hell and Stockmayer, Klages and Heilmann, Thiele and Balhorn, etc. See bibliography.

² Elaise : Compt. rend., **132**, 38.

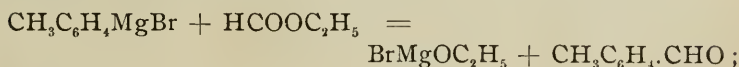


This, with dilute acids, yields $\text{R.CO.R}'$.

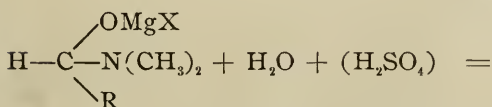
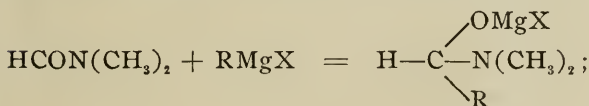
Béis made ketones by the reactions :¹



Several different ways of making aldehydes have been discovered. Gattermann and Maffezzeoli² used the reaction :



Bouveault³ allowed dimethylformamide to react with magnesium organic halides according to the equations :

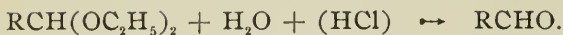
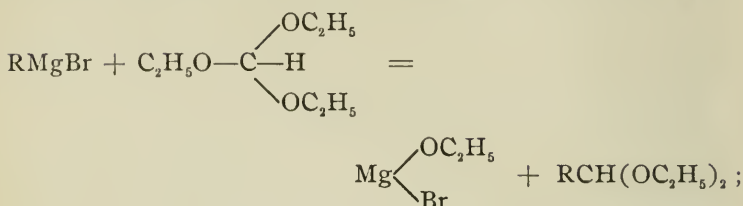


¹ Compt. rend., 137, 575 (1903).

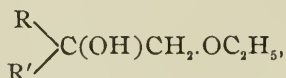
² Ber. d. chem. Ges., 36, 4152 (1903).

³ Compt. rend., 137, 756 (1903).

With the esters of orthoformic acid we get the reactions :¹



Starting with $\text{RCO}.\text{CH}_2.\text{OC}_2\text{H}_5$ and $\text{R}'\text{MgBr}$ we can get

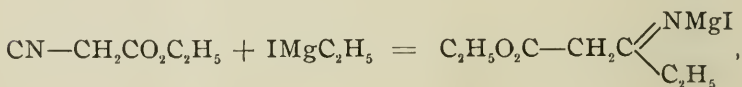


this yields the aldehyde,



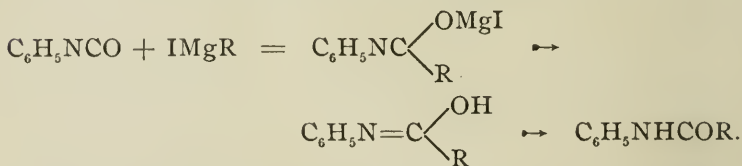
when dehydrated by heating with anhydrous oxalic acid.²

The reactions of the organo-magnesium halides with different classes of nitrogen compounds have been studied, in some cases with very interesting results. The production of ketones and aldehydes has just been mentioned. Ketone esters are obtained from cyan esters, for instance :



and this, with water, gives $\text{C}_2\text{H}_5\text{O}_2\text{C}-\text{CH}_2\text{CO}.\text{C}_2\text{H}_5$.

When isocyanates are used we get anilides :³

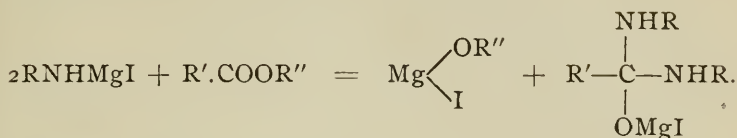


¹ Tschitschibabin : J. Russ. Phys. Chem. Ges., **35**, 222; Ber. d. chem. Ges., **37**, 186 (1904). Bodroux : Bull. Soc. Chim., [3], **31**, 585 (1904).

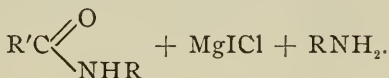
² Béal et Sommelet : Compt. rend., **138**, 89; Bull. Soc. Chim., [3], **31**, 300 (1904).

³ Blaise : *Loc. cit.*

Anilides were also prepared from esters.¹

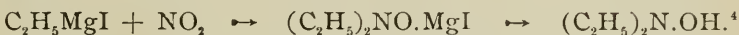
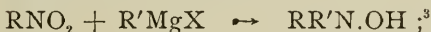


This, with dilute hydrochloric acid, yields

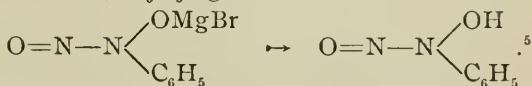
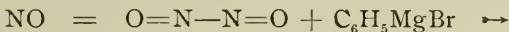


Sachs and Loevy studied the reaction with the mustard oils,² obtaining, as we should expect, the thioanilides, or in general, the thioacylamines, R.NHCSR' .

Hydroxylamine derivatives are formed when nitrogen peroxide, or nitro compounds, are allowed to act upon organo-magnesium halides :

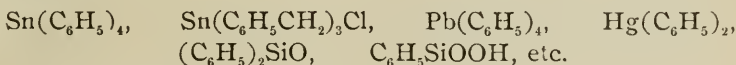


With nitric oxide we have the reaction :



A number of more complex reactions have been carried out with other nitrogen compounds.⁶

The Grignard reaction has been found to be applicable to the formation of alkyl and aryl derivatives of certain metals. Compounds of tin,⁷ lead and mercury,⁸ thallium⁹ and silicon¹⁰ have been made. A few of these are represented by the formulas,



¹ Bodroux : Compt. rend., 138, 1427.

² Ber. d. chem. Ges., 36, 585; 37, 874.

³ Moureu : Compt. rend., 132, 837 (1901).

⁴ Wieland : Ber. d. chem. Ges., 36, 2315 (1903).

⁵ Sand u. Singer : Ann. Chem. (Liebig), 329, 190 (1903).

⁶ See bibliography.

⁷ Pfeiffer u. Schnurmann : Ber. d. chem. Ges., 37, 319.

⁸ Pfeiffer u. Truskier : *Ibid.*, 37, 1125.

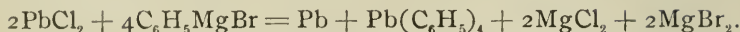
⁹ Meyer u. Bertheim : *Ibid.*, 37, 2051.

¹⁰ Dilthey u. Eduardoff : *Ibid.*, 37, 2051.

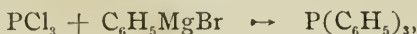
Some of the typical reactions are given :



and



Similar reactions take place with the trichloride and oxychloride of phosphorus.¹



and



This comparatively brief summary of the work that has been done in this field will give at least an idea of the possibilities of the Grignard reaction. Only its more general applications have been discussed, but a study of the bibliography will show how wide these are and will suggest new lines of investigation.

In the bibliography which follows an attempt has been made to give references to all articles bearing on the subject, including those in which the method was used to prepare compounds for other lines of work. It is brought down to February 21, 1905.

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¹ Sauvage : Compt. rend., **139**, 674.

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SCHROETER : Ueber die Einwirkung von Kohlensäure auf Phenylmagnesium ; **36**, 3005 (1903).

HOUBEN : Eine neue Synthese von Kohlenwasserstoffen mittels magnesiumorganischer Verbindungen ; **36**, 3083 (1903).

HOUBEN : Ueber die Einwirkung von Chlorkohlensäureester auf Alkylmagnesiumhaloide ; **36**, 3087 (1903).

SACHS u. LOEVY : Berichtigung über Tribenzylcarbinol ; **36**, 3236 (1903).

WERNER : Eine neue Synthese von Kohlenwasserstoffen mittels magnesiumorganischer Verbindungen ; **36**, 3618 (1903).

GATTERMANN u. MAFFEZEOLI : Ueber die Darstellung von Aldehyden aus Organomagnesiumverbindungen ; **36**, 4152 (1903).

FREUND : Zur Kenntniss des Cotarnins ; Anwendung der Grignard'schen Reaction auf dasselbe ; **36**, 4257 (1903).

BRÜHL : Neuere Versuche über Camphocarbonsäure ; **36**, 4272 (1903).

EHRlich u. SACHS : Die Darstellung von Triphenylmethanfarbstoffen aus Brommagnesiumdimethylanilin als Vorlesungsversuch ; **36**, 4296 (1903).

TSCHITSCHIBABIN : Eine neue allgemeine Darstellungsmethode der Aldehyde ; **37**, 186 (1904).

HELL u. STOCKMAYER : Ueber Anisyl-phenyl-propen ; **37**, 225 (1904).

HELL u. BAUER : Aromatische Propenverbindungen ; Diphenyl-propen und Phenyl-methyl-propen ; **37**, 230 (1904).

PFEIFFER u. SCHNURMANN : Beitrag zur Darstellung von Alkyl- und Aryl-Zinnverbindungen ; **37**, 319 (1904).

SACHS u. LUDWIG : Ueber die Einwirkung magnesiumorganischer Verbindungen auf alkylirte Phthalimide ; **37**, 385 (1904).

HELL : Ueber eine einfache Bildung von Stilben, Mono-4-methoxystilben und α -Methylstilben ; **37**, 453 (1904).

HOUBEN : Zur Synthese von Kohlenwasserstoffen mittels magnesiumorganischer Verbindungen und Methylsulfat ; **37**, 488 (1904).

HOUBEN : Ueber die Einwirkung magnesiumorganischer Verbindungen auf Lactone ; **37**, 489 (1904).

BÜNZLY u. DECKER : Ueber einige Ammoniumverbindungen ; Synthese eine Oxydihydrobase ; **37**, 575 (1904).

ACREE : Ueber α -Naphthyl-magnesium-bromid ; **37**, 625 (1904).

KLAGES u. SAUTTER : Ueber optischactive Benzolkohlenwasserstoffe ; 37, 649 (1904).

BAUER : Zur Darstellung von Dialkylphthaliden ; 37, 735 (1904).

BRÜHL : Metallorganische Synthesen der Acylcampher ; 37, 746 (1904).

HARRIES u. WEIL : Ueber 2,6-Dimethyl-heptadien-2,5-diozonid ; 37, 845 (1904).

TSCHITSCHIBABIN : Ueber den Hexahydro-*m*-toluylaldehyd ; 37, 850 (1904).

SACHS u. LOEVY : Ueber die Einwirkung von magnesiumorganischer Verbindungen auf die Senföle und Isonitrile ; 37, 874 (1904).

ACREE : Ueber *o*-, *m*-, und *p*-Tolyl-diphenyl-carbinol ; 37, 990 (1904).

WAGNER, MOYCHO u. ZIENKOWSKI : Zur Kenntniss des Camphers ; 37, 1032 (1904).

SCHROETER : β -Methyl-zimmtsäure ; 37, 1090 (1904).

PFEIFFER u. TRUSKIER : Zur Darstellung organischer Blei- und Quecksilberverbindungen ; 37, 1125 (1904).

HELL u. BAUER : Aromatische Propenverbindungen, IV ; Isoeugenol-äthyläther ; 37, 1128 (1904).

DILTHEY u. EDUARDOFF : Ueber die Darstellung von Phenylsiliciumverbindungen ; 37, 1139 (1904).

KLAGES u. HEILMANN : Arylirte Äthylene und ihre Reduction zu Arylparaffinen ; 37, 1447 (1904).

THIELE u. BALHORN : Ueber einen chinoïden Kohlenwasserstoff ; 37, 1463 (1904).

ODDO : Metallorganische Synthesen in der Camphergruppe ; 37, 1569 (1904).

SACHS u. STEINERT : Zur Kenntniss des *p*-Dimethylamino-benzaldehydes ; 37, 1733 (1904).

ULLMANN u. SCHLAEPFER : Ueber Derivate des Hexaphenyl-*p*-xylols ; 37, 2001 (1904).

MEYER u. BERTHEIM : Alkylverbindungen des Thalliums ; 37, 2051 (1904).

TSCHELINZEFF : Ueber die Analogie zwischen den organischen Sauerstoff- und Stickstoff-Verbindungen ; 37, 2081 (1904).

HEIDE : Diazoessigester und Systeme mit conjugirten Doppelbindungen ; 37, 2101 (1904).

ROSENHEIM u. SINGER : Die Darstellung von Alkylsulbinsäuren ; 37, 2152 (1904).

BRÜHL : Untersuchungen in der Camphergruppe, I ; 37, 2156, 2163 (1904).

KLAGES : Zur Kenntniss der Styrole ; 37, 2301 (1904).

ULLMANN u. ENGI : Ueber 9-Diphenylxanthen ; 37, 2367 (1904).

DILTHEY u. LAST : Ueber die Einwirkung von Arylmagnesiumhalogeniden auf Dicarbonsäuren ; 37, 2639 (1904).

BUSCH : Ueber das Verhalten magnesiumorganischer Verbindungen zu Benzylanilin ; 37, 2691 (1904).

ACREE : Ueber einige Synthesen mit Hilfe von Phenylnatrium und Alkylmagnesiumbromiden ; 37, 2753 (1904).

BUNZLY u. DECKER: Ueber Xanthonium- und Thioxanthonium Verbindungen; **37**, 2931 (1904).

SACHS u. SACHS: Das Verhalten tertiärer Amine gegen magnesiumorganischer Verbindungen; **37**, 3088 (1904).

BAEYER u. VILLIGER: Dibenzalaceton und Triphenylmethan; **37**, 3191 (1904).

SACHS, v. WOLFF u. LUDWIG: Die Einwirkung magnesiumorganischer Verbindungen auf alkylierte Saccharine; **37**, 3252 (1904).

SACHS u. THONET: Ueber Oxyfuchsone; **37**, 3326 (1904).

FREUND: Versuche zur Herstellung von Alkaloiden der Isochinolinreihe; **37**, 3334 (1904).

DECKER u. PSCHORR: Ueber die Einwirkung von Benzylmagnesiumchlorid auf Cyclaminone; **37**, 3396 (1904).

FEHLENBERG: Zur Kenntniss der Einwirkung von Magnesiummethyljodid auf Mesityloxyd und Phoron; **37**, 3578 (1904).

HOUBEN: Die Uebertragung der Kolbe'schen Salicylsäuresynthese auf stickstoffhaltige Benzolabkömmlinge; **37**, 3978 (1904).

KLAGES: Ueber die Reduction ungesättigter Phenoläther durch Natrium und Alkohol; **37**, 3987 (1904).

STOERMER u. SIMON: Ueber geometrische Isomerie bei Derivaten des Diphenyläthyläthers; **37**, 4163 (1904).

HELL u. HOFFMANN: Ueber das 4-Methoxyphenyläthylcarbinol; **37**, 4188 (1904).

FREUND: Verfahren zur Darstellung solcher Verbindungen, welche sich von den Pseudobasen durch Ersatz der Hydroxylgruppe gegen Kohlenwasserstoffreste herleiten; **37**, 4666 (1904).

FREUND u. BECK: Ueber eine Reihe neuer, vom Dihydroberberin sich herleitender Basen; **37**, 4673 (1904).

FREUND u. BECK: Einwirkung von Benzylmagnesiumchlorid auf Krystallviolet; **37**, 4679 (1904).

FRANKE u. KOHN: Die Einwirkung magnesiumorganischer Verbindungen auf β -Oxyaldehyde und auf Ketonalkohole; **37**, 4730 (1904).

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C. E. WATERS.

OBITUARY.

ALFRED HENRY ALLEN.

Alfred H. Allen, F.C.S., F.I.C., was born at Southwark, London, January 17, 1846, and died at Sheffield, July 14, 1904. He received his professional education at the College of Chemistry and Agriculture, Kennington and at the Royal

College of Chemistry and School of Mines (now the Royal College of Science), under Hofmann, Tyndall and Percy and at University College, London. Shortly afterwards he settled in Sheffield. Allen's activity was many-sided, he was a successful teacher, was Borough and County Analyst and had a large private practice. His time and energy were given ungrudgingly to the service of the Society of Public Analysts, Institute of Chemistry and Society of Chemical Industry, in each of which he held high office for many years. Allen is, perhaps, best known in this country for his "Commercial Organic Analysis," which is easily the standard work on its subject. It is not a mere compilation, but contains the results of numerous original investigations made by the author and his assistants. He also wrote "Chemistry of the Urine," 1895, embodying his study of diabetes, from which he was suffering; in addition he was a frequent contributor to the analytical and technical journals. Allen's geniality and kindness were combined with a wonderful memory, keenness of intellect and great ability for the rapid grasp of intricate questions.

REVIEWS.

MATERIALIEN DER STEREOCHEMIE. In Form von Jahresberichten. II Bände. Bearbeitet von C. A. Bischoff. 1904. pp. cxxxvi + 1977. Braunschweig: Vieweg und Sohn.

This work may be considered as a supplement to the two volumes of Bischoff's "Handbuch der Stereochemie," which have previously been reviewed.¹

The book is in two volumes, of about two thousand pages and is made up of nine annual reports on stereochemistry, embracing the years 1894-1902. As its name implies it is intended chiefly for reference and maintains the cyclopedic character of the original "Handbuch."

Each year's report is divided into four sections, treating of general stereochemistry, optical isomerism, the geometrical isomerism of optically inactive bodies and the relations between positions in space and chemical reactions.

Under the section of general stereochemistry are included monographs and special publications dealing with stereochemical problems. The literature on the optical rotation of active organic compounds is very thoroughly reviewed in the second section. A systematic enumeration of the many examples of geometrical isomerism is given in section III. Inorganic compounds, occurring in more than one form, are also given here. Section IV., which treats of space relations in chem-

¹ THIS JOURNAL, 16, 475; 17, 725.

ical reactions, also includes a list of all known ring formations, organic and inorganic. Separate chapters in this section are devoted to molecular rearrangements, substitution- and addition-reactions, "Abspaltungen" und "Verkettungen."

Those who have not followed closely the progress of stereochemistry will be surprised to learn that so extensive a work could be written upon investigations in this subject, concerning which nothing was heard twenty years ago.

In some chapters the literature references are very complete, while in others they are decidedly lacking. One would not expect to see the American literature on molecular rearrangements completely ignored; more attention to it would greatly increase the value of the book. No references are given to the numerous publications on this subject by Stieglitz, Ransom and Wheeler and his co-workers, which have appeared since 1894.

The reviewer observed several typographical errors, as was to be expected in a work of such magnitude. On page 1203 the formula of *formylphenylestiger* is represented as $\text{HCO} \cdot (\text{C}_6\text{H}_5)\text{CHCOOC}_6\text{H}_5$ instead of $\text{HCO}(\text{C}_6\text{H}_5)\text{CHCOOC}_2\text{H}_5$. The names of American writers have been misspelled in many instances, as is of common occurrence in German books.

Regardless of defects in the work, few chemists will fail to find it suggestive. Those who are especially interested in stereochemistry will find the book indispensable.

T. B. JOHNSON.

A SYSTEMATIC HANDBOOK OF VOLUMETRIC ANALYSIS, or the Quantitative Estimation of Chemical Substances by Measure, Applied to Liquids, Solids and Gases. Adapted to the Requirements of Pure Chemical Research, Pathological Chemistry, Pharmacy, Metallurgy, Manufacturing Chemistry, Photography, etc., and for the Valuation of Substances used in Commerce, Agriculture and the Arts. By FRANCIS SUTTON, F.I.C., F.C.S., Public Analyst for the County of Norfolk, etc. Ninth edition, revised and enlarged. Philadelphia: P. Blakiston's Son & Co. 1904. pp. xii + 617.

Sutton's "Volumetric Analysis" has so long been a valued reference book that comment upon its general character is obviously superfluous. The present (ninth) edition has been printed from new plates and the text has been revised throughout. The size of the page is slightly larger and, although the number is less than in the last edition, the changes have resulted in a net increase of reading matter. These are so widely distributed throughout the text that a few only of the more striking can properly be enumerated.

The most extensive additions appear to be found in the paragraphs which treat of the examination of ammoniacal gas liquors, contributed by the Chief Inspector under the

Alkali-Works Regulation Acts and his assistant (pp. 77-82 and p. 502); in the section upon the azo dyes, nitro and nitroso compounds, etc., contributed by Dr. E. Knecht (pp. 366-367); in the description of Procter's modification of Hehner's method of estimating the hardness of waters (pp. 503-507) and in the account of the work of L. W. Andrews on the uses of potassium iodate (pp. 507-510). Other additions, as, for example, the description of the titration of iron by means of titanous chloride, the volumetric determination of magnesium, the extended description of the determination of free alkali in soap, or, on the other hand, the omission of certain methods which the author has come to distrust or consider obsolete (the Grossman-Böhlig method for the examination of salt-cake, for example) are at least an equally important part of the attempt to keep the handbook abreast of the times.

The index has been revised and extended and this work appears to have been well done, although one consults it in vain to discover the different uses made of titanous chloride, a somewhat unfamiliar agent as yet and also for the names of the originators of a considerable number of the processes mentioned in the text. But these are minor matters, the fact that the present edition has followed the eighth, after an interval of only four years, indicates the general high esteem in which the manual is held.

H. P. TALBOT.

A TEXT-BOOK OF QUANTITATIVE CHEMICAL ANALYSIS BY GRAVIMETRIC, ELECTROLYTIC, VOLUMETRIC AND GASOMETRIC METHODS, with Seventy-two Laboratory Exercises giving the Analysis of Pure Salts, Alloys, Minerals and Technical Products. By J. C. OLSEN, A.M., PH.D., Professor of Analytical Chemistry in the Polytechnic Institute of Brooklyn. New York: D. Van Nostrand Company. 1904. pp. xix + 513.

This text-book is stated by the author to have been born of a spirit of discontentment with the previously existing manuals of analytical chemistry, because of the tendency of them to give special prominence to some one branch of the subject to the exclusion of others, thus necessitating reference, on the part of the thoughtful student, to a "very considerable number of text-books and journals." To avoid this perversion of time and energy the attempt has been made to present a work which shall accord to each branch of the subject—such as gravimetric, volumetric, electrolytic and gasometric analysis—a treatment which shall correspond with its relative importance from a practical standpoint and also to present a book which shall meet the author's own views as to desirable sequence of topics, while it likewise acquaints the student with the underlying

reasons for each step taken and develops his technical skill. It is avowedly written, in the first instance, as a text-book from which to teach.

The first two chapters deal with the general operations of chemical analysis and contain much timely advice; then follow thirteen chapters (154 pp.) dealing with gravimetric methods and including thirty-nine "laboratory exercises" (analytical procedures), which range in difficulty, though not strictly progressively, from the determination of water of crystallization to complete analyses of such alloys as Rose's metal, or those of complex silicates. Electrolytic methods are next dealt with in two chapters (27 pp.), followed by ten chapters (129 pp.) of volumetric methods, after which the analysis of iron, steel and coal, water analysis, the analysis of fats and oils, gas analysis and stoichiometry, each are treated in a single chapter (116 pp. in all); the whole ends with an appendix containing useful tables. Of the laboratory exercises not mentioned above, six comprise electrolytic methods, twenty-four volumetric procedures and the other two include the proximate analysis of coal and the analysis of illuminating gas.

Any attempt to produce a text-book of analytical chemistry which shall present a "thorough" and "comprehensive" view of the subject within the scope of the present volume seems, of itself, to invite criticism and it may fairly be questioned whether, looked at from a general standpoint, Professor Olsen has succeeded better than some of his predecessors in producing a well-balanced work. This should not imply, however, that there is not a great deal in his treatment of the subject that is worthy of the attention of all who are interested in the training of students in the art of chemical analysis, nor does it mean that the more experienced analyst will fail to find useful suggestions. Opinions must always differ as to the most desirable sequence in the presentation of topics to a class and, still more, as to the choice of detailed procedures. In these particulars the reader will quite likely find more to praise than to censure, but it is not so clear that in the chapters relating to specialized topics, such as gas analysis, water analysis, or the examination of oils, fats and waxes, the student will find such a treatment as will preclude that necessity for reference to more extended treatises which the author sought to avoid, nor does it seem reasonable that this should be so.

In the chapter devoted to stoichiometry, a phase of laboratory instruction, which is too often neglected is brought into desirable prominence and the subject-matter is presented in a

helpful way. Most of the procedures and explanations throughout the book are given with painstaking detail, but the work is uneven in this respect and in some cases, the directions, as given, would almost certainly lead to erroneous results. One such instance is found on p. 317, where, in the description of the determination of iron in its ores, the student is directed to add mercuric chloride solution to a *hot* solution containing a greater or less excess of stannous chloride. Reduction to metallic mercury would follow, which, in turn, would react upon the potassium dichromate used, obscuring the end-point of the titration.

The publishers cannot be congratulated upon the typography of this volume. Imperfect letters, inverted letters and crooked lines occur with unpleasant frequency throughout its pages. Other letters are missing, no less than five figures are lacking altogether in the logarithm table and the word phosphorus is frequently and uniformly misspelled throughout more than half of the volume. Carelessness in these matters has been noticeable in several recent works from different publishing houses, but in none to a greater extent than in this volume; it seems quite time that there should be a return to the old-time pride both in freedom from errors and in excellence of appearance.

But it may properly be said that Professor Olsen has contributed a volume to the literature of analytical chemistry which is of distinct interest from the teachers' standpoint and is worthy of the attention of his co-laborers.

H. P. TALBOT.

ELEMENTARY MANUAL FOR THE CHEMICAL LABORATORY. By LOUIS WARNER RIGGS, PH.D., Instructor of Chemistry in Cornell University. First edition. New York: John Wiley and Sons. 1904.

This is a laboratory guide for those students who need to cover the ground of general chemistry, qualitative analysis and volumetric analysis in one year. The author describes the chemical changes in qualitative analysis in terms of the electrolytic dissociation theory. The work on volumetric analysis precedes that on qualitative analysis; other teachers will agree with the author in preferring this sequence.

E. R.

THE INDUSTRIAL AND ARTISTIC TECHNOLOGY OF PAINT AND VARNISH. By ALVAH HORTON SABIN, Chemist, Edward Smith & Co. First Edition. New York: John Wiley and Sons. 1904. Cloth, 8vo. pp. vi + 364.

The author treats the subject more from the standpoint of the manufacturer and engineer than from that of the chemist.

The technology of varnish is the especial feature of the book and will be welcomed by those desiring general information on the subject. Varnish has usually been made behind closed doors and methods and mixtures guarded as trade secrets.

It is shown here, however, that the quality of the product is due to a knowledge of the requirements and to experience and care used in its manufacture.

The chapters on metal corrosion and protective coatings deal with the general causes of oxidation and means of prevention.

Results of an extended series of exposure tests of protective coatings, in salt and fresh water, are given and bear out, in general, the author's opinion regarding the durability of oleo resin varnishes and enamel paints.

The methods employed in making these tests can be studied to advantage, as it is difficult to secure comparable results in this line of investigation.

The thorough review of the early paint and varnish literature adds materially to the bibliography of the subject.

The author states that the present knowledge of the chemistry of resin gums is too indefinite to give a satisfactory method of analysis for oleo resin varnishes, so the analyst will gain but little new chemical data, except indications for lines of investigation.

Unfortunately, there is a lack of definite information on this subject and it is especially regretted that the author, with his knowledge as a chemist and manufacturer, should not have devoted more space to the chemistry of the fossil and recent resin gums and the changes which take place when they are melted and mixed with the oil in the varnish kettle.

This is a line of investigation of especial interest to the technical chemist and one which has received but scant attention in the literature.

The subject-matter is handled in a clear and readable manner, with evidence of the author's dry humor and pleasant personality; the index is good and the text free from typographical errors.

S. S. VOORHEES.

AMERICAN CHEMICAL JOURNAL

THE REACTION BETWEEN UNSATURATED COM- POUNDS AND ORGANIC MAGNESIUM COM- POUNDS.

V. REACTIONS WITH α -CYANCINNAMIC ACID.

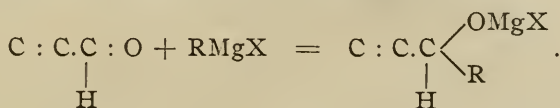
BY E. P. KOHLER AND MARIE REIMER.

The unsaturated compounds that were considered in the previous papers of this series have essentially the same structure—all contain the “conjugated system,”



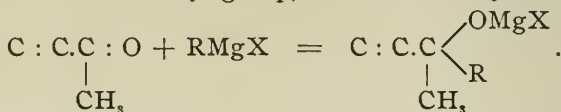
For the sake of comparison with the more complicated case, represented by cyancinnamic ester, the results obtained with these substances may be briefly summarized as follows :

1. The reaction between unsaturated aldehydes and organic magnesium compounds invariably consists in the addition of the magnesium derivative to the carbonyl group :¹

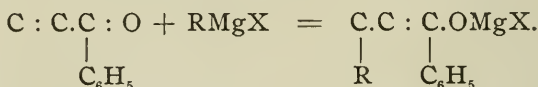


¹ THIS JOURNAL, 31, 642.

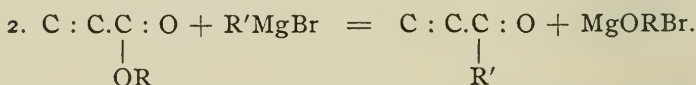
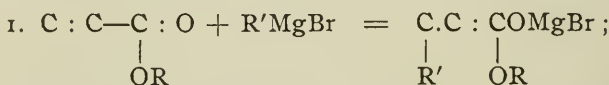
2. Ketones that have methyl in combination with the carbon atom of the carbonyl group, react like aldehydes :¹



3. The reaction with ketones having phenyl in combination with the carbon atom of the carbonyl group, consists in 1,4-addition of the magnesium compound to the ketone :²

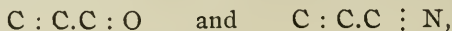


4. With esters two different reactions may take place: 1,4-addition and replacement of the alkoxyl with an alkyl group :³



With aromatic magnesium compounds the principal reaction is that represented by the first equation; with aliphatic magnesium derivatives that represented by the second; but the result also depends upon the atoms or groups in the α -position with reference to the carbonyl group. "Negative" groups in this position increase the extent to which the first⁴ reaction takes place.

α -Cyancinnamic ester contains two conjugated systems,



in the relation to each other, which Thiele⁵ has called "crossed." According to Thiele the points at which combination takes place, in compounds having this structure, depends upon the specific properties of the combining substances. In the case

¹ THIS JOURNAL, 31, 658.

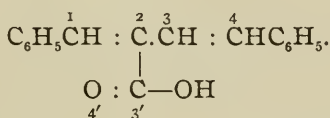
² *Ibid.*, 31, 649.

³ *Ibid.*, 33, 21.

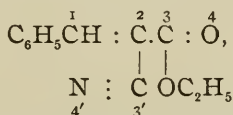
⁴ *Ibid.*, 33, 153.

⁵ Ann. Chem. (Liebig), 306, 111.

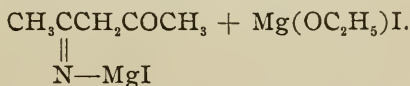
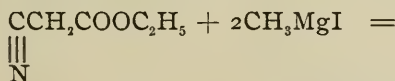
of dibenzalpropionic acid, for example, bromine combines with the carbon atoms marked $\overset{1}{\text{C}}$ and $\overset{4}{\text{C}}$, while hydrogen, which forms stable compounds with oxygen, combines at the points marked $\overset{1}{\text{C}}$ and $\overset{4'}{\text{O}}$:



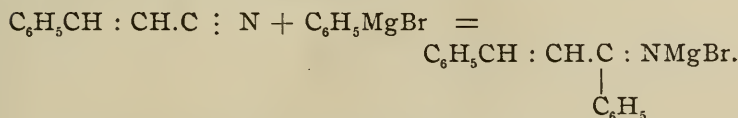
Of the two systems present in cyancinnamic ester,



the first, as shown above, takes up organic magnesium compounds in the 1,4-positions. All that is known of the second is that the cyanogen, like the carbonyl group, readily combines with Grignard's reagent. Blaise found, for example, that the reaction between ethyl cyanacetate and methylmagnesium iodide is represented by the equation:

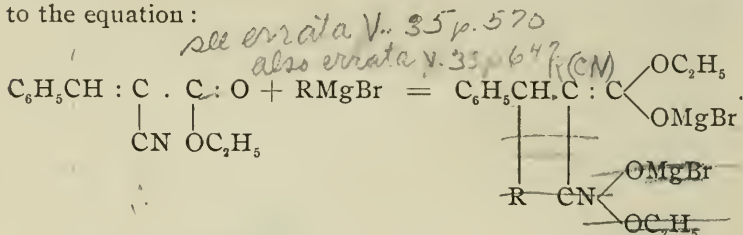


To determine whether this system can take up organic magnesium compounds by 1,4-addition, we treated cinnamionitrile and phenylcinnamionitrile with phenylmagnesium bromide. The former reacts according to the equation:



The latter, in which the reactivity of the cyanogen group is diminished by the presence of phenyl in the α -position, does not react at all. The cyanogen group in α -cyancinnamic ester

should, therefore, have no influence on the addition-reactions of the substance. This conclusion is in perfect agreement with the facts. Cyancinnamic ester, although it contains two conjugated systems and two groups capable of reacting with organic magnesium compounds, always reacts, solely, according to the equation :



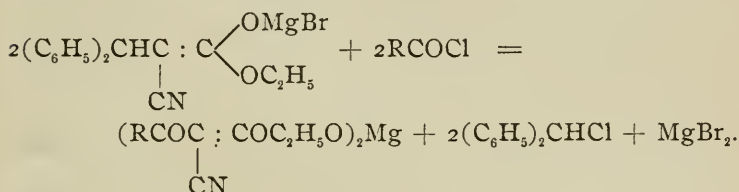
It is the first unsaturated ester that gives the same reaction with all classes of magnesium compounds; the cyanogen group in the α -position completely prevents the replacement of alkoxyl by alkyl.

The effect of different groups in the α -position is shown by the following table :

Ester.	Magnesium compound.	Per cent of product formed by replacement of OR.	Per cent of product formed by 1,4-addition.
$\text{C}_6\text{H}_5\text{CH} : \text{CHCOOR}$	$\text{C}_6\text{H}_5\text{MgBr}$	50	50
"	CH_3MgI	100	0
$\text{C}_6\text{H}_5\text{CH} : \text{CCOOR}$	$\text{C}_6\text{H}_5\text{MgBr}$	30	70
 Br			
"	CH_3MgI	100	0
$\text{C}_6\text{H}_5\text{CH} : \text{CCOOR}$	$\text{C}_6\text{H}_5\text{MgBr}$	0	100
 C_6H_5			
"	CH_3MgI	100	trace
$\text{C}_6\text{H}_5\text{CH} : \text{CCOOR}$	$\text{C}_6\text{H}_5\text{MgBr}$	0	100
 CN			
"	CH_3MgI	0	100

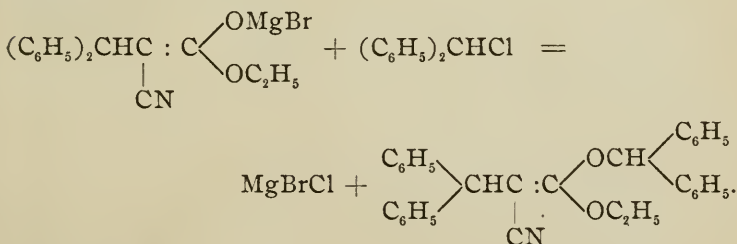
The magnesium compound obtained by adding phenylmagnesium bromide to cyancinnamic ester behaves, towards most

reagents, like the corresponding substances prepared from other unsaturated compounds. The reaction with acid chlorides, however, is totally different from that of any other magnesium compound that we have studied. If the substance is added to excess of the acid chloride, the diphenylmethyl group is smoothly replaced by an acyl group :



This remarkable reaction is a perfectly clean one and we have not succeeded in getting any intermediate products.

The same reaction takes place when the operation is reversed, so that the acid chloride is added to an excess of the magnesium derivative, but in this case the diphenylchloromethane subsequently reacts with another molecule of the magnesium compound :



The resulting substance is an acetal of a new type of unsaturated ketones and we hope that, by suitable selection of materials, it may be possible to get the ketones themselves.

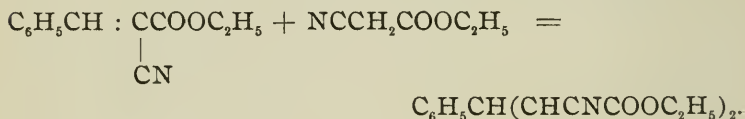
EXPERIMENTAL.

Preparation of Ethyl α-Cyancinnamate.—The ester was first obtained by Carrick,¹ by condensing benzaldehyde with cyanacetic ester. Carrick used a small quantity of sodium alcoholate as a condensing agent and found that the yield is poor,

¹ J. prakt. Chem., [2], 45, 501.

unless the reaction is carried out with very small quantities and, even then, rarely exceeds 60 per cent of the calculated amount. As a by-product he obtained an oil from which no pure substances could be isolated. The ester was subsequently made by Fiquet,¹ by condensing benzaldehyde with cyanacetic acid and saturating an alcoholic solution of the product with hydrochloric acid. This gives a fair yield, but involves a tedious purification of benzalcyanacetic acid.

We have found that the ester can be obtained, in calculated quantity, by a slight modification of Carrick's method. It seemed likely, in view of the results published by Knoevenagel and by others who have studied the action of alkaline condensing agents, that the by-product described by Carrick was a benzylidene compound, formed by condensation of cyancinnamic ester with a second molecule of cyanacetic ester:



Knoevenagel has shown that this second reaction can usually be avoided by condensing at sufficiently low temperatures. We therefore adopted the following procedure: A solution of 100 grams benzaldehyde and 100 grams ethyl cyanacetate, in 200 cc. of alcohol (95 per cent), that has previously been distilled from a small quantity of potassium hydroxide, is cooled in a freezing-mixture. The condensing agent—1 gram of sodium dissolved in absolute alcohol—is added to the solution when the temperature is at or below -15° . If the temperature is sufficiently low the liquid remains colorless and, in the course of a few hours, cyancinnamic ester begins to separate in long, colorless needles. After 24 hours, during which the temperature is allowed to rise, gradually, to 0° , the reaction is complete. The mixture is then cooled to -15° , the ester filtered and washed with a small quantity of cold alcohol. The weight of crude ester is 180 grams and a little more can be obtained by neutralizing the filtrate and distilling it in a current of steam. Alcohol and a small quantity of oil pass over, while

¹ Ann. Chim. Phys., [6], 29, 443.

the ester remains and solidifies on cooling. It was purified by recrystallization from alcohol.

Reaction with Phenylmagnesium Bromide.—In the earlier experiments an ethereal solution of ester was added, drop by drop, to a solution of the bromide, cooled in ice-water. Under these conditions each drop of the solution produces a yellow precipitate, that slowly redissolves, on shaking, until the liquid contains a little more than 1 molecule of ester for 2 molecules of the magnesium compound. At this point the yellow precipitate no longer disappears.

In the later experiments an ethereal or benzene solution of ester was added to a boiling solution of the magnesium compound, as it was found that the product is the same as that formed at low temperatures. When the reaction takes place in boiling solution, the intermediate yellow product disappears almost as fast as it forms and the reagents can be used in equivalent quantities. From ether the addition-product separates as a stiff paste, from benzene as an oil that remains emulsified in the liquid and is, therefore, much better adapted for subsequent reactions.

Ethyl α-Cyan-β,β-diphenylpropionate,
 $(C_6H_5)_2CHCH(CN)CO_2C_2H_5$.—When the magnesium compound,

obtained as described above, is decomposed with water, the product is ethyl cyandiphenylpropionate. It is easily purified by recrystallization from alcohol and the yield is good—20 grams of cyancinnamic ester, with the phenylmagnesium bromide obtained from 2.75 grams of magnesium, gave 25.4 grams of pure ester; calculated 27.9 grams. The ester crystallizes from alcohol in large, colorless pyramids, melting at 78°. It is readily soluble in chloroform, acetone and boiling alcohol; moderately in cold alcohol and in ether; very slightly in ligroin. Analysis:

0.1890 gram substance gave 0.5362 gram CO_2 and 0.1059 gram H_2O .

	Calculated for $C_{15}H_{17}O_2N$.	Found.
C	77.69	77.37
H	6.11	6.22

As the ester contains a mobile hydrogen atom in the α -position, it is very easily hydrolyzed by alcoholic potassium hydroxide. In the cold the action of the base is confined, almost exclusively, to the ethoxyl group; in boiling solution it also includes the cyanogen group.

Cyandiphenylpropionic Acid, $(C_6H_5)_2CHCHCO_2H$.—A strong,



aqueous solution of potassium hydroxide, containing a little more than 1 equivalent of the base, was added to a cold, saturated solution of the ester, in absolute alcohol. After the mixture had stood for 2 days, at the ordinary temperature, the alcohol was evaporated in a current of air, the residue poured into water and the resulting liquid extracted with ether. The ethereal solution contained only a small quantity of unchanged ester. From the aqueous solution hydrochloric acid precipitated a colorless liquid, that solidified on standing. The solid was recrystallized from a mixture of ether and ligroin. Analysis:

0.1610 gram substance gave 0.4506 gram CO_2 and 0.0782 gram H_2O .

	Calculated for $C_{16}H_{13}O_2N$.	Found.
C	76.49	76.33
H	5.18	5.40

The acid crystallizes in small, colorless needles, melting at 162° . It is very soluble in alcohol and ether; slightly in ligroin and in boiling water.

β,β -Diphenylpropionitrile, $(C_6H_5)_2CHCH_2CN$.—When cyandiphenylpropionic acid is heated it begins to lose carbon dioxide at about 185° . Five grams of the acid were heated at 190° , in a sulphuric acid bath, until there was no further gas evolution. The yellow residue solidified on cooling and was recrystallized from low-boiling ligroin, until the melting-point re-

maintained constant at 100°. Analysis showed that the substance was diphenylpropionitrile.

0.1711 gram substance gave 0.5471 gram CO₂ and 0.0986 gram H₂O.

	Calculated for C ₁₅ H ₁₃ N.	Found.
C	86.95	87.13
H	6.28	6.40

The nitrile dissolves readily in most organic solvents and has a pronounced tendency to separate from solution as an oil. From low-boiling ligroin it crystallizes in small, lustrous prisms.

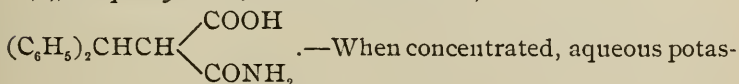
β,β-Diphenylpropionamide, (C₆H₅)₂CHCH₂CONH₂. — This was easily obtained by boiling the corresponding nitrile, with alcoholic potassium hydroxide, for ½ hour, with a return condenser; the alcohol was removed by distillation and the residue poured into water. The solid that separated melted sharply at 127°, after one recrystallization from aqueous alcohol. Analysis:

0.1901 gram substance gave 0.5603 gram CO₂ and 0.1129 gram H₂O.

	Calculated for C ₁₅ H ₁₅ O ₂ N	Found.
C	80.20	80.37
H	6.66	6.59

The amide is readily soluble in alcohol and ether, very slightly so in water. It crystallizes in needles. Boiling potassium hydroxide hydrolyzes it very slowly to the corresponding acid. With a concentrated aqueous solution the hydrolysis was complete after boiling for 8 hours, while, with concentrated alcoholic potassium hydroxide, it was incomplete even after 12 hours. The resulting acid—*β,β*-diphenylpropionic acid—was identified by comparison with a specimen from another source.

β,β-Diphenylmethylmalonic Monamide,



sium hydroxide was added to a hot, concentrated solution of ethyl cyandiphenylpropionate, a colorless potassium salt precipitated. This was probably a metallic derivative of the ester, as it redissolved almost immediately. After boiling the solution for several hours the alcohol was evaporated and the solid residue acidified with dilute acid. To separate non-acid products, the precipitate was dissolved in solution of sodium carbonate. A small quantity of insoluble material was removed, the filtrate extracted with ether and the acid reprecipitated. It was colorless, but so unstable that it was difficult to get it free from diphenylpropionamide. It was dried in the air, then dissolved in boiling, absolute alcohol and the solution immediately cooled in a freezing-mixture. The acid separated in long, fine needles. These were washed with ether and dried in a current of air. Analysis:

0.1492 gram substance gave 0.3898 gram CO_2 and 0.0815 gram H_2O .

	Calculated for $\text{C}_{16}\text{H}_{15}\text{O}_3\text{N}$.	Found.
C	71.37	71.09
H	5.58	6.06

The acid is readily soluble in alcohol, moderately in ether. It loses carbon dioxide so easily that the melting-point observed depends largely upon the rate at which the temperature is raised. The highest melting-point—obtained by rapid heating—was 170° . In an air-bath it slowly loses carbon dioxide and ultimately liquefies at 130° . The decomposition can be completed, in a short time, by heating to 150° . The product is diphenylpropionamide, identical with that of the hydrolysis of diphenylpropionitrile. It is noteworthy that the carbamide group has a much more pronounced effect upon a carbonyl group in combination with the same carbon atom than the cyanogen group has.

Ethyl α,α -Bromcyan- β,β -diphenylpropionate,
 $(\text{C}_6\text{H}_5)_2\text{CHCBrCNCO.OC}_2\text{H}_5$.—The reaction between bromine and the magnesium compound, obtained by adding phenylmagnesium bromide to cyancinnamic ester, is like that between bromine and the addition-products from other unsatura-

ted compounds. The bromine reacts as fast as it is added, until the liquid contains 2 atoms for every atom of magnesium used in the preparation of phenylmagnesium bromide. The product, separated in the usual way, crystallized in large, colorless prisms. Analysis :

0.1971 gram substance gave 0.4372 gram CO_2 and 0.0885 gram H_2O .

	Calculated for $\text{C}_{18}\text{H}_{16}\text{O}_2\text{N}$.	Found.
C	60.33	60.49
H	6.47	4.95

The ester melts at 97° . It is readily soluble in chloroform and acetone, moderately in absolute alcohol and ether. Cold, alcoholic potassium hydroxide hydrolyzes it and simultaneously eliminates all bromine as hydrobromic acid.

see errata p. 647
 α -Cyan- β,β -diphenylcinnamic Acid, $(\text{C}_6\text{H}_5)_2\text{C} : \text{C}(\text{CN})\text{CO}_2\text{H}$, and β,β -diphenylcinnamitrile, $(\text{C}_6\text{H}_5)_2\text{C} : \text{CH} : \text{CN}$.—Concentrated, aqueous solution of potassium hydroxide was added to bromcyandiphenylpropionic ester, suspended in a small quantity of absolute alcohol, which was cooled in ice-water. The liquid immediately became yellow and, in a short time, a mixture of potassium bromide and a potassium salt of an organic acid began to crystallize. After the mixture had stood in an ice-chest for 10 hours it was poured into water. This dissolved the salts, but left a considerable quantity of oil, which was removed by ether.

From the aqueous solution hydrochloric acid precipitated a solid that contained nitrogen, but was free from bromine. The acid was purified by recrystallization from a mixture of chloroform and ligroin. Analysis :

0.1654 gram substance gave 0.4660 gram CO_2 and 0.0650 gram H_2O .

	Calculated for $\text{C}_{16}\text{H}_{11}\text{O}_2$.	Found.
C	77.11	76.87
H	4.43	4.36

see errata p. 647
Cyanodiphenylcinnamic acid is readily soluble in alcohol, ether and chloroform, sparingly so in ligroin and boiling water. It

crystallizes in needles, melting at 178° . Above 190° it decomposes, with evolution of carbon dioxide. When boiled with alcoholic potassium hydroxide part is transformed into β, β -diphenylcinnamic acid, but most of it simply loses carbon dioxide and passes into diphenylcinnamionitrile. The yield of acid is poor—less than 30 per cent of the calculated amount.

The ethereal extract, on evaporation, left an oil that slowly solidified. At ordinary temperatures this substance always separated from solution as an oil, but it could be recrystallized by dissolving it in methyl alcohol, cooling in a freezing-mixture and adding a particle of the solid. It was thus obtained in long, pale-yellow needles, melting sharply at 49° .

0.2114 gram substance gave 0.6790 gram CO_2 and 0.1047 gram H_2O .

	Calculated for $\text{C}_{15}\text{H}_{11}\text{N}$.	Found.
C	87.80	87.59
H	5.36	5.50

It is difficult to hydrolyze the nitrile. No acid was obtained by boiling it with alcoholic potassium hydroxide for 8 hours. It was, therefore, heated at 135° , for 8 hours, with this reagent; most of it was recovered unchanged, a small quantity decomposed into benzophenone, carbon dioxide and ammonia and a still smaller quantity—5 per cent—was hydrolyzed to β, β -diphenylpropionic acid.

Action of Acetyl Chloride on the Addition-product.—A solution of acetyl chloride, in benzene, was added, drop by drop, to the magnesium compound, suspended in boiling benzene. Each drop of the solution produced a precipitate, which separated as a paste, but speedily turned into a hard, granular solid. It soon became apparent that this action of acetyl chloride is quite different from that of acid chlorides on the magnesium compounds that have been studied heretofore, because only half as much chloride reacted as in previous cases, where 1 molecule of chloride was required for every atom of magnesium present.

As soon as the chloride was present in excess, the boiling liquid was filtered through glass wool and the precipitate

see extract p. 647.

washed thoroughly with boiling benzene. The solid insoluble in benzene was an organic magnesium compound which contained nitrogen but no halogen. It was slowly decomposed by boiling aqueous alcohol and did not crystallize well from absolute alcohol. It was, however, obtained in pure, well-defined crystals by diluting the solution, in boiling absolute alcohol, with one-fifth of its volume of hot water and immediately chilling the liquid in a freezing-mixture. It separated very slowly in small, shining prisms. Analysis:

0.2011 gram substance gave 0.3347 gram CO_2 , 0.1022 gram H_2O and 0.0212 gram MgO .

	Calculated for $(\text{C}_7\text{H}_5\text{O}_3\text{N})_2\text{Mg} \cdot 2\text{H}_2\text{O}$.	Found.
C	45.60	45.38
H	5.43	5.64
Mg	6.62	6.36

The water of crystallization could not be determined separately. The substance does not lose in weight below 140° and begins to change color above this temperature.

When the compound was digested with dilute hydrochloric acid, the magnesium dissolved as chloride, leaving an oil that solidified in ice-water and then melted at 26° . Analysis indicated that this was ethyl cyanacetate:

0.1601 gram substance gave 0.3170 gram CO_2 and 0.0857 gram H_2O .

	Calculated for $\text{C}_7\text{H}_9\text{O}_3\text{N}$.	Found.
C	54.19	53.99
H	5.81	5.94

It was completely identified by making the copper salt and comparing this with a known specimen. The magnesium compound is, therefore, ethyl magnesium cyanacetate.

The filtrate from the preceding substance was evaporated on the water-bath. The oily residue solidified on standing and was purified by recrystallization from a mixture of chloroform and alcohol. Analyses:

I. 0.1523 gram substance gave 0.4640 gram CO_2 and 0.0861 gram H_2O .

II. 0.1510 gram substance gave 0.4621 gram CO_2 and 0.0840 gram H_2O .

III. 0.5478 gram substance gave 16.8 cc. moist N at 26° and 752 mm.

IV. 0.5600 gram substance gave 16.7 cc. moist N at 25° and 755 mm.

	Calculated for $\text{C}_{81}\text{H}_{27}\text{O}_2\text{N}$.	I.	II.	Found. III.	IV.
C	83.57	83.17	83.45	. .	. .
H	6.07	6.28	6.25	. .	.
N	3.15	. .	. .	3.45	3.30

The molecular weight was determined in boiling acetone:

$$C = 1710.$$

Solvent. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
51.25	0.4387	0.035	418
	1.0310	0.087	381
	1.9030	0.158	409

Calculated for $\text{C}_{81}\text{H}_{27}\text{O}_2\text{N}$.	Found.
445	403

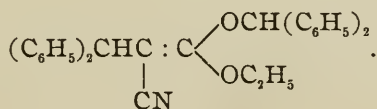
The substance is readily soluble in chloroform and in boiling glacial acetic acid, moderately so in boiling alcohol and acetone, very slightly in cold alcohol and in ether. It melts at 156° and does not decompose below 300° .

Chemically, the substance is extremely inert. It reacts neither with methylmagnesium iodide nor with phosphorus pentachloride, therefore contains no hydroxyl. It gives neither an oxime nor a hydrazone, hence, probably, contains no carbonyl group. It does not combine with bromine, does not reduce boiling solution of potassium permanganate and is not reduced by zinc and acetic acid. It dissolves in concentrated sulphuric acid, giving a yellow color, but water reprecipitates it. It is very slowly decomposed by boiling alcoholic potassium hydroxide. After boiling for 3 days we succeeded in isolating, from the product, small quantities of diphenylpropionic acid and benzhydrol ether; but most of it consisted of a gum with which nothing could be accomplished.

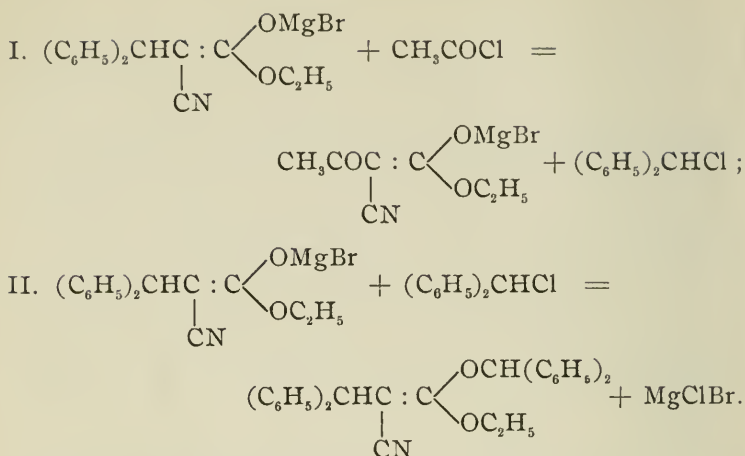
A much cleaner decomposition was obtained by heating the substance with concentrated hydrochloric acid, for 8 hours, at 225°. There was considerable pressure in the tube, the gas consisted of carbon dioxide and a substance that burned with a green flame, possibly ethyl chloride. The other products were diluted with water and steam distilled. The first portion of the distillate gave iodoform with an alkaline solution of iodine, showing that the substance contains an ethoxyl group. A solid, that separated from the distillate, was recrystallized from alcohol. Its melting-point, 111°, composition and properties agreed with those of benzhydrol ether and a comparison with a specimen made from benzhydrol showed that the two were identical.

The residue in the distilling-flask was extracted with ether and the ethereal solution, in turn, with solution of sodium carbonate. From this dilute hydrochloric acid precipitated diphenylpropionic acid. The ether, on evaporation, left only a minute quantity of highly colored oil. The aqueous solution that had been extracted with ether, was evaporated to dryness. The residue was ammonium chloride, free from organic matter, showing that there is no alkyl group in combination with nitrogen.

These products of decomposition, diphenylpropionic acid, benzhydrol ether, alcohol, carbon dioxide and ammonia lead to the formula :



The formation of such a substance can be understood by assuming that the acid chloride first replaces the diphenylmethyl group, by acetyl and that the resulting diphenylchlormethane subsequently reacts with a second molecule of the magnesium compound :



If this hypothesis be correct, it ought to be possible to make the same substance by treating the magnesium compound, directly, with diphenylchloromethane. This experiment was tried, but diphenylbrommethane was used instead of the chlorine compound, because the latter is not easily prepared. An ethereal solution of diphenylbrommethane (10 grams) was added, gradually, to the magnesium compound obtained from 1 gram of magnesium, 8 grams of brombenzene and 7 grams of ethyl cyancinnamate. The mixture was boiled for $\frac{1}{2}$ hour, then poured into iced hydrochloric acid. The crystalline solid that separated was recrystallized from a mixture of chloroform and alcohol. It melted at 156° and was, in every respect, like the substance described above. The yield was excellent, 16 grams instead of 18.3 grams calculated. This method of synthesis leaves no doubt as to the structure of the substances under consideration. It also furnishes the best of evidence that the reaction between unsaturated esters and organic magnesium compounds really consists in 1,4-addition, as has been assumed in all the papers of this series.

Further evidence as to the mechanism of the reaction by which the compound, m. p. 156° , was formed, was obtained by reversing the mode of procedure and adding the magnesium compound to excess of the acidic chloride. According to

the hypothesis made above, all of the magnesium compound should, under these conditions, be transformed into magnesium ethyl cyanacetoacetate. This was found to be the case. A suspension of the magnesium compound, obtained in the usual way and containing 2.5 grams of metal, was siphoned into a dry benzene solution of acetyl chloride (12 grams). The solid that separated was filtered and recrystallized as before. It was magnesium cyanacetoacetic ester. The filtrate did not contain a trace of the substance melting at 156°. After evaporating the ether and benzene in a draught, the residue was poured into boiling water. The resulting solid was benzhydrol ether, probably formed by the action of water on diphenylchlormethane.

Reaction between the Magnesium Compound and Benzoyl Chloride.—The reaction was carried out like that with acetyl chloride. Ethyl magnesium cyanbenzoylacetate separated as a paste, that gradually became granular. The substance is readily soluble in aqueous alcohol, from which it crystallizes in long, silky needles containing water of crystallization. When the recrystallized salt was digested with dilute hydrochloric acid, until all the magnesium had dissolved, there remained an oil that solidified on cooling. It was recrystallized from a mixture of ether and ligroin and melted at 46°—the melting-point of ethyl cyanbenzoylacetate. It gave a beautiful green copper salt with copper acetate and sodium hydroxide.

The filtrate from ethyl magnesium cyanbenzoylacetate contained only the substance melting at 156°. The amount corresponded, almost exactly, to half the ethyl cyancinnamate used. 21.5 grams instead of 22.3 grams, from 20 grams of ethyl cyancinnamate. The experiment was also carried out in the opposite way—the magnesium compound being siphoned into excess of the acidic chloride. The only products were ethyl magnesium cyanbenzoyl acetate and benzhydrol ether.

Reaction with α-Naphthylmagnesium Bromide.

Ethyl α-Cyan-β,β-naphthylphenylpropionate,

$$\begin{array}{c} \text{C}_{10}\text{H}_7 \\ \text{C}_6\text{H}_5 \end{array} \left. \begin{array}{l} \diagup \\ \diagdown \end{array} \right\} \text{CHCHCO}_2\text{C}_2\text{H}_5 \text{—The mode of procedure was the same}$$

$$\begin{array}{c} | \\ \text{CN} \end{array}$$

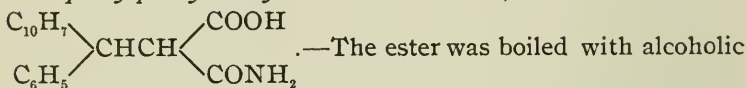
as that adopted for phenylmagnesium bromide. The ester was purified by recrystallization from alcohol.

0.1786 gram substance gave 0.5244 gram CO_2 and 0.0977 gram H_2O .

	Calculated for $\text{C}_{22}\text{H}_{18}\text{O}_2\text{N}$.	Found.
C	80.24	80.07
H	5.77	6.07

The ester is readily soluble in chloroform and ethyl acetate, moderately so in boiling alcohol and acetone, slightly in ether. It crystallizes from alcohol in aggregates of minute plates, melting at 132° .

Naphthylphenylmethylmalonic Monamide,



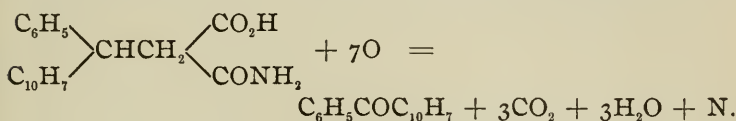
potassium hydroxide for two hours. The alcohol was evaporated, the residue dissolved in water and the solution extracted with ether, to remove a small quantity of colored products. The solid, precipitated by acidifying the extracted solution, was colorless, but only partly soluble in sodium carbonate. Like the corresponding phenyl compound, the acid loses carbon dioxide when it is liberated from its salts. The product, obtained by recrystallizing the precipitated acid from alcohol, also contained some naphthylphenylpropionamide, but, by extracting it repeatedly with small quantities of boiling absolute alcohol and drying the residue at the ordinary temperature, the pure acid was obtained. It then gave a perfectly clear solution in sodium carbonate. Analysis :

0.1468 gram substance gave 0.3806 gram CO_2 and 0.0726 gram H_2O .

	Calculated for $\text{C}_{20}\text{H}_{17}\text{O}_3\text{N}$.	Found.
C	70.50	70.70
H	5.33	5.49

When the acid is heated rapidly, in a capillary tube, it melts and decomposes at 170° – 180° ; heated slowly, in an open vessel, it begins to lose carbon dioxide below 135° . In alkaline solution it has scarcely any action on boiling potassium per-

manganate solution ; in acid solution the permanganate is reduced rapidly. A quantity of the substance was oxidized by suspending it in water, that was kept at the boiling-point by a rapid current of steam and adding acid solution of permanganate. The steam carried over an oil that solidified in the condenser. After crystallization from aqueous alcohol, the solid melted at 75° . As it gave a sublimate of naphthalene, when heated with soda lime, it was α -naphthophenone,

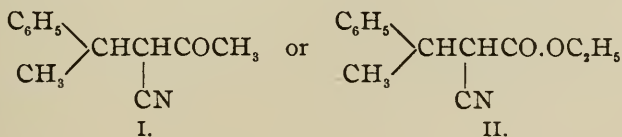


Reaction with Methylmagnesium Iodide.

Ethyl α -Cyan- β -phenylbutyrate, $\text{CH}_3\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$.—The

substances were brought together in cold, ethereal solution. The product, isolated in the usual way, was an oil which could not be induced to solidify. Five grams of it were suspended in dilute solution of sodium carbonate and treated with solution of potassium permanganate, as long as reduction took place in the cold. After dissolving the oxides of manganese with sulphur dioxide, a current of steam was passed through the liquid. An oil having the odor of acetophenone passed over. It was extracted with ether, the ether evaporated and the residue treated with benzaldehyde and a few drops of alcoholic sodium hydroxide. Benzalacetophenone, identified by comparison with a specimen from other sources, crystallized from the mixture.

As the oil gave acetophenone on oxidation, it was evident that ethyl cyancinnamate, unlike the esters described in previous papers, does not give a tertiary alcohol when it reacts with methylmagnesium iodide. The product must be a ketone or an ester :



An alcoholic solution of the oil was allowed to stand with benzaldehyde and sodium alcoholate, but it gave no unsaturated ketone. The oil, therefore, does not contain the ketone represented by I.

A small quantity of it was boiled with concentrated, aqueous potassium hydroxide and the distillate collected in solution of potassium carbonate, containing iodine. Iodoform was formed, showing that the oil contains an ester, as represented by II.

α-Cyan-β-phenylbutyric Acid, $\text{CH}_3\text{CH} \begin{array}{c} | \\ \text{C}_6\text{H}_5 \end{array} \text{CHCO}_2\text{H}$. — Concen-

trated, aqueous potassium hydroxide was added, in small quantities, to an alcoholic solution of the oil, until the mixture remained alkaline after standing for several hours. On cooling in a freezing-mixture a potassium salt separated, in colorless crystals. This was filtered, washed with absolute alcohol and dissolved in a small quantity of water. From the solution, hydrochloric acid precipitated cyanphenylbutyric acid, as an oil that solidified on standing in contact with the acid liquid. It was dried and dissolved in chloroform, from which it crystallizes in compact, colorless prisms, melting at 130° . Analyses :

I. 0.1625 gram substance gave 0.4158 gram CO_2 and 0.0860 gram H_2O .

II. 0.1683 gram substance gave 0.4310 gram CO_2 and 0.0891 gram H_2O .

	Calculated for $\text{C}_{11}\text{H}_{13}\text{O}_2\text{N}$.	I.	Found. II.
C	69.82	69.78	69.86
H	5.80	5.88	5.88

The acid has a pronounced tendency to separate from solution as an oil. It is readily soluble in alcohol, ether and chloroform, sparingly so in ligroin. It loses carbon dioxide when heated at 180° .

Methylphenylmethylmalonic Monamide,

$\text{C}_6\text{H}_5 \begin{array}{c} \diagup \\ \text{CH} \end{array} \text{CH} \begin{array}{c} \diagdown \\ \text{CH} \end{array} \begin{array}{c} \text{COOH} \\ \text{CONH}_2 \end{array}$. — The potassium salt of this acid was obtained when ethyl cyanphenylbutyrate, or the corresponding

acid, was boiled for several hours with alcoholic potassium hydroxide. It was purified by recrystallization from aqueous alcohol.

0.1477 gram substance gave 0.3456 gram CO_2 and 0.0860 gram H_2O .

	Calculated for $\text{C}_{11}\text{H}_{13}\text{O}_3\text{N}$.	Found.
C	63.84	63.82
H	6.28	6.46

The acid crystallizes in coarse needles and melts, with decomposition, at 172° .

β -Phenylbutyramide, $\text{CH}_3\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CONH}_2$, was obtained by heating the preceding acid, at 180° , until evolution of carbon dioxide ceased. The residue solidified on cooling. It was deposited from very dilute alcohol in fine, white needles.

0.1534 gram substance gave 0.4128 gram CO_2 and 0.1106 gram H_2O .

	Calculated for $\text{C}_{10}\text{H}_{13}\text{ON}$.	Found.
C	73.62	73.58
H	7.97	8.05

The amide is very soluble in alcohol and ether, slightly so in ligroin and in boiling water. It melts at 105° .

β -Phenylbutyric Acid, $\text{CH}_3\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CO}_2\text{H}$. — Phenylbutyramide, like diphenylpropionamide, is hydrolyzed with the greatest difficulty. In order to get a substance that was free from nitrogen it was necessary to boil the amide with concentrated potassium hydroxide for 2 days. The product was isolated in the usual way, but it invariably separated from solution as an oil, that remained liquid in a freezing-mixture. It was, therefore, converted into the sodium salt, which was recrystallized from boiling alcohol, in which it is moderately soluble; on cooling it separates in minute plates, containing water of crystallization. Analyses:

I. 0.2262 gram salt lost 0.0202 gram H_2O at 150° .

II. 0.2276 gram salt gave 0.0783 gram Na_2SO_4 .

	Calculated for $\text{C}_{10}\text{H}_{11}\text{O}_2\text{Na}$.	I.	Found.	II.
H_2O	11.27	11.17	.	.
Na	8.84	.	.	8.93

Reaction with Benzylmagnesium Chloride.—The reaction was carried out at low temperatures, but the product was far from homogeneous. This was probably due, largely, to the fact that a number of substances are formed when magnesium is dissolved in ethereal solution of benzyl chloride. The oily product was suspended in water and distilled with steam, which removed some toluene and a considerable quantity of dibenzyl. The residue was again extracted with ether, the ethereal solution dried over sodium sulphate and the ether allowed to evaporate at a low temperature. As the product again separated as an oil it was hydrolyzed without further purification.

β,γ -Diphenylethylmalonic Monamide,

$$\begin{array}{c} \text{C}_6\text{H}_5\text{CH}_2 \\ \text{C}_6\text{H}_5 \end{array} \text{CHCH} \begin{array}{c} \text{CO}_2\text{H} \\ \text{CONH}_2 \end{array}$$
 .—The oily ester was boiled with alcoholic potassium hydroxide for several hours, the resulting acid isolated in the usual way and purified by recrystallization from aqueous alcohol. Analysis:

0.1575 gram substance gave 0.4144 gram CO_2 and 0.0750 gram H_2O .

	Calculated for $\text{C}_{17}\text{H}_{17}\text{O}_3\text{N}$.	Found.
C	72.08	71.88
H	6.00	5.89

The substance is readily soluble in alcohol and ether, sparingly so in boiling water. It crystallizes from aqueous alcohol in very fine needles. When heated rapidly it melts, with decomposition, at about 182° ; heated slowly it loses carbon dioxide and melts at a much lower temperature.

The acid rapidly reduced acid potassium permanganate solution. A current of steam that was passed through the liquid carried over an oil, which solidified in the receiver. After recrystallization from aqueous alcohol it melted at 60° and was identified as desoxybenzoine, by comparison with a specimen made from benzyl. These results prove that benzylmagnesium chloride and ethyl cyancinnamate yield ethyl α -cyan- β,β -phenylbenzylpropionate.

β-γ-Diphenylbutyramide, $\text{CH}_2(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CONH}_2$.

—The acid described above was heated at 185° , until carbon dioxide ceased to be evolved. The residue ultimately solidified, when allowed to stand in contact with ligroin. It almost invariably separates from solution as an oil, that solidifies very slowly on standing in contact with some of the solid. It can, however, be recrystallized by dissolving it in cold water containing a small quantity of alcohol and allowing this solution to evaporate. It separates in long, thick needles, melting at 62° .

0.1441 gram substance gave 0.4231 gram CO_2 and 0.0934 gram H_2O .

	Calculated for $\text{C}_{16}\text{H}_{17}\text{ON}$.	Found.
C	80.33	80.07
H	7.10	7.20

Reaction with Isopropylmagnesium Bromide.

Ethyl α-Cyan-β-phenyl-γ,γ-dimethylbutyrate,

$\begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array} \text{CH} \text{CH}(\text{C}_6\text{H}_5)\text{CH}(\text{CN})\text{CO}_2\text{C}_2\text{H}_5$.—The reaction was car-

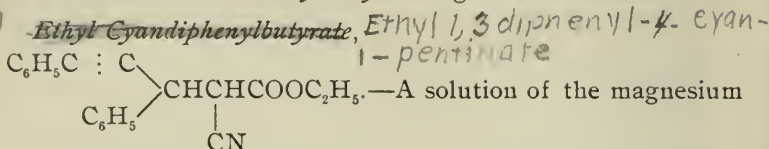
ried out in the cold. The product, treated in the usual way, gave an oil. The hydrocarbons were removed by steam distillation and residue boiled, for 2 hours, with alcoholic potassium hydroxide. After evaporating the alcohol, the solid obtained was completely soluble in water, showing that the original product contained neither ketone nor tertiary alcohol. From the aqueous solution hydrochloric acid precipitated an oil, that solidified on standing in contact with the acid solution. It was recrystallized from dilute aqueous alcohol and deposited in fine needles.

0.1720 gram substance gave 0.4190 gram CO_2 and 0.1121 gram H_2O .

	Calculated for $\text{C}_{18}\text{H}_{19}\text{O}_3\text{N}$.	Found.
C	66.38	66.43
H	7.23	7.24

When heated rapidly, in a capillary tube, it melts, with decomposition, at 176° .

Reaction with Phenylacetylenemagnesium Bromide.



compound was prepared as follows: Five grams of magnesium were dissolved in 25 grams of ethyl bromide and 100 cc. of ether. Twenty grams of phenylacetylene were added and the mixture boiled, with an inverted condenser, until there was no further evolution of ethane.

Ethereal solution of ethyl cyancinnamate was added to the cold solution of the magnesium compound, as long as the yellow precipitate that first formed redissolved on vigorous shaking. The addition-product separated as a stiff, colorless paste. When this was poured into iced hydrochloric acid a considerable quantity of crystalline ester separated. The remainder was obtained by separating and evaporating the ethereal layer. The yield was excellent. The ester was purified by recrystallization from alcohol. Analysis:

0.1557 gram substance gave 0.4500 gram CO_2 and 0.0810 gram H_2O .

	Calculated for $\text{C}_{20}\text{H}_{17}\text{O}_2\text{N}$.	Found.
C	79.20	78.81
H	5.61	5.78

The ester crystallizes in colorless needles, melting at 80° . It is readily soluble in boiling alcohol, moderately so in cold alcohol and in ether.

CHEMICAL LABORATORY,
 BRYN MAWR COLLEGE,
 December, 1904.

CAMPHORIC ACID.

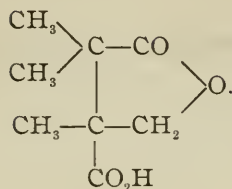
[FOURTEENTH PAPER.]

BY WILLIAM A. NOYES.

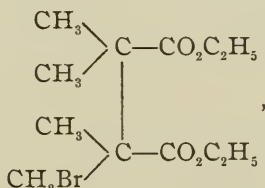
Derivatives of Trimethylparaconic Acid.

Some time ago Dr. Patterson and I reported a synthesis of trimethylparaconic acid,¹

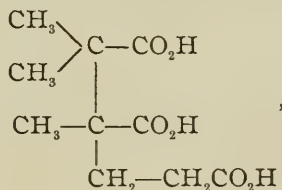
¹ THIS JOURNAL, 28, 238.



At the time it was hoped that, from this, it would be easy to obtain ethyl bromtetramethylsuccinnate,



from which compound, by condensation with malonic ester, followed by saponification of the resulting product and the loss of carbon dioxide by the acid formed, it should be a simple matter to prepare the inactive homocamphoric acid,



corresponding to the active acid of Forster and Lapworth.¹

The beautiful synthesis of camphoric acid by Komppa² has deprived the contemplated synthesis of much of its interest, but it has seemed, nevertheless, worth while to continue the work. Unexpected difficulties were encountered, however, in the first step outlined above and it is, as yet, very uncertain if the way to overcome these has been discovered, although a large amount of time has been spent on the problem. The fact that I cannot, personally, continue the work³ makes it de-

¹ J. Chem. Soc., **75**, 986.

² Ber. d. chem. Ges., **46**, 4332.

³ Through the aid of the Carnegie Institution, Dr. H. W. Doughty will pursue the investigation in conjunction with me.

sirable to give an account of what has already been accomplished.

Preparation of Ethyl Dimethylcyansuccinnate.—Bone and Sprankling¹ advise the use of a pressure-bottle in the condensation of ethyl bromisobutyrate with ethyl cyanacetate. I have found that, by using a more concentrated solution of sodium ethylate, even better yields than they record can be obtained, at atmospheric pressure. Twenty-two grams of sodium were dissolved in 230 cc. of absolute alcohol, by boiling for some time with an upright condenser; 109 grams of ethyl cyanacetate and 188 grams of ethyl bromisobutyrate were added and the mixture was heated 5–6 hours in a boiling water-bath. This gave 157 grams, or 72 per cent of the theory, of ethyl dimethylcyansuccinate, boiling at 150°–170°, under low pressure. The conversion to ethyl trimethylcyansuccinate and saponification to trimethylsuccinic acid were carried out essentially as described by Bone and Sprankling.²

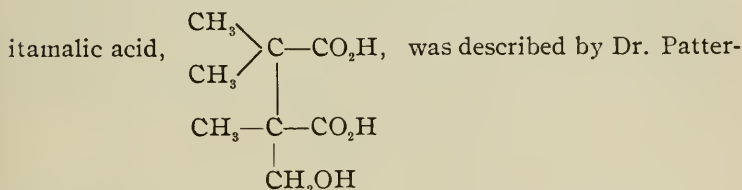
Preparation of Trimethylparaconic Acid.—The methods described by Dr. Patterson and myself have been somewhat modified, as the result of further experience. Thirty-five grams of sodium trimethylsuccinnate, dried at 150°–175°, were finely powdered and added to 6.5 grams of trioxymethylene, prepared by evaporating a 40 per cent solution of formaldehyde on the water-bath and drying the residue in a vacuum desiccator. This mixture was introduced into a sealing-tube, in portions of 4 grams, with alternate portions of 2.6 cc. of freshly distilled acetic anhydride. The tube was heated at 180°–200°, for 6–7 hours, or till the contents were completely fluid while hot. After cooling, the tube opened with slight pressure. The mixture again liquefied on warming and was dissolved in 300 cc. of hot water. After standing over night, the solution was filtered from tarry matters and the filtrate concentrated to about 100 cc. On the addition of 60 cc. of concentrated hydrochloric acid, the larger part of the trimethylparaconic acid was precipitated and was nearly pure, after

¹ J. Chem. Soc., 75, 854.

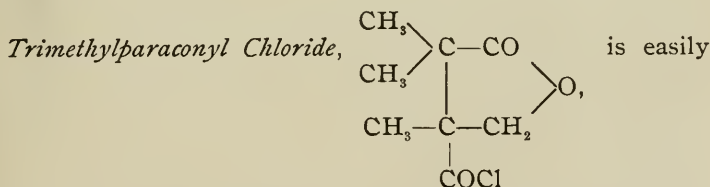
² Loc. cit.

washing till free from sodium chloride. A few grams of the acid may be obtained from the filtrate by extraction with ether. The total yield may be from 85-90 per cent of the theory, or just about equal to the weight of the trimethylsuccinic acid used. The acid is purified by crystallizing from water. It melts at 270° (cor.).

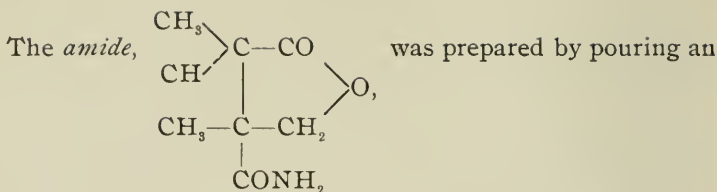
The preparation of the sodium and silver salts of trimethyl-



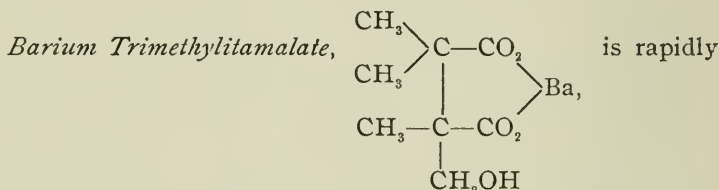
son and myself. By treatment of the latter with ethyl iodide, we obtained what was probably the diethyl ester of trimethylitamalic acid. This was, however, a viscous oil, which could not be purified and its composition differs so little from that of the ethyl ester of trimethylparaconic acid that an analysis was considered useless. When this ester was treated with phosphorus tribromide a product, nearly free from bromine, was obtained, which consisted chiefly of *ethyl trimethylparaconate*. This was prepared, later, in a number of different ways. When pure it crystallizes in needles, melting at 34° - 35° and boiling at 150° - 152° (23 mm.).



prepared by warming the acid gently with phosphorus pentachloride and volatilizing the phosphorus oxychloride under low pressure. The chloride may also be distilled under diminished pressure, if care be taken to prevent its solidification in the exit-tube. After crystallizing from dry ether it melts at 139° - 140° and decomposes, only slowly, in contact with water.



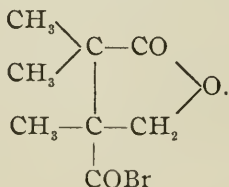
etheral solution of the chloride into 10 per cent ammonia. It is very difficultly soluble in water, alcohol, ether or benzene. When prepared as stated it melts at 241° – 243° . After crystallizing from water or alcohol the melting-point is lower, probably because of partial hydrolysis. Analysis gave 8.25 per cent N. Calculated, 8.19 per cent.



formed when trimethylparaconic acid is heated with an excess of barium hydroxide solution. It is difficultly soluble, 100 parts of water dissolving, approximately, 0.55 gram of the salt. The air-dried salt lost only a trifling amount in weight at 140° . Analysis gave 42.04 per cent Ba. Calculated, 42.22 per cent.

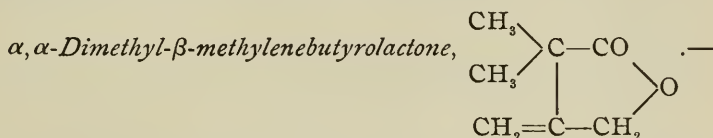
Trimethylparaconic anhydride and *acetyl trimethylitamalic anhydride* will be described below.

Having failed in the preparation of ethyl bromtetramethyl succinnate (see above) an attempt was made to secure a bromine derivative by heating trimethylparaconyl chloride with 1 molecule of bromine, in sealed tubes. At 100° – 120° the action of the bromine was very slow indeed, while at temperatures above 140° the material was soon carbonized. After many trials the only product obtained was the bromide,

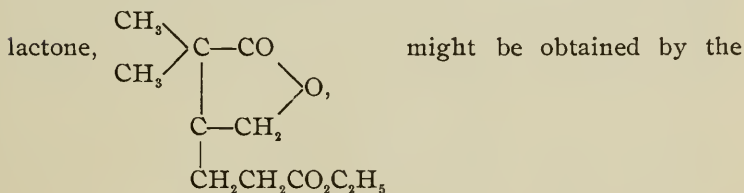


This is difficultly soluble in ether and melts at 125° , after crystallizing from that medium. Analysis gave 34.08 and 34.06 per cent bromine. Calculated, 34.04 per cent.

When 2.5 grams of the bromide were heated with 2 cc. of absolute alcohol, at a temperature raised gradually to 230° , during 3 hours, about 1.2 grams of ethyl trimethylparaconate and a considerable quantity of regenerated acid were obtained. It had been hoped that ethyl bromtetramethylsuccinate might be formed, by a reaction similar to that which takes place so readily with other lactones.



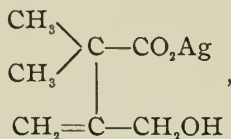
It was thought possible that ethyl trimethylhydroxyadipate



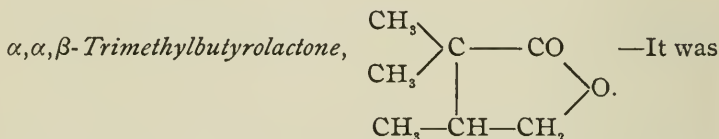
electrolysis of a mixture of potassium trimethylparaconate and potassium ethyl succinate, by the method which Crum Brown and Walker used so successfully in the preparation of ethyl adipate. When electrolyzed with a diaphragm, the chief product was regenerated trimethylparaconic acid. When electrolyzed in a platinum crucible, without a diaphragm, using a current of 4 amperes and 9-10 volts, for 4 hours, a mixture of esters was obtained. This contained, of course, a considerable amount of ethyl adipate. A small quantity of higher boiling products was also formed, but no definite compound was separated from these. There was produced, however, a small quantity of dimethylmethylene butyrolactone. This compound is an oil, difficultly soluble in water and volatile with steam. An alkaline solution decolorizes potassium perman-

ganate instantly, indicating the unsaturated character of the compound.

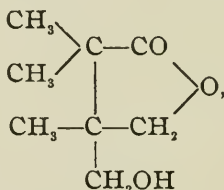
The *silver salt* of the corresponding hydroxy acid,



crystallizes in needles, which are difficultly soluble in cold water. Analysis gave 43.34 per cent Ag. Calculated, 43.03 per cent.



hoped that the reduction of ethyltrimethylparaconate by sodium and absolute alcohol¹ might give the compound

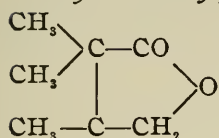


which could, doubtless, be used for the synthesis desired. The only definite product that could be isolated, after reduction, was *αα,β-trimethylbutyrolactone*. Approximately 4 grams of this were obtained from 22 grams of the ester. It is a solid, which melts at 37° and boils at 211°–212°. Analysis :

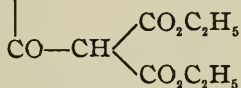
	Calculated for C ₇ H ₁₂ O ₂ .	Fond.
C	65.63	65.36
H	9.37	9.56

The silver salt of the corresponding hydroxy acid gave : Ag 42.89 per cent. Calculated, 42.68 per cent.

¹ Bouveault : Compt. rend., 136, 1676 ; 137, 60.

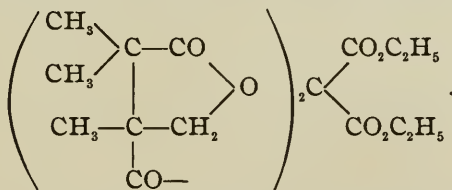
Ethyl Trimethylparaconylmalonate,

—This compound was prepared in



the hope that, by the reduction of the carbonyl group to methylene, the product could be utilized for the desired synthesis.

Two and three-tenths grams of sodium were finely divided, by melting in xylene and shaking vigorously. After pouring off the xylene and rinsing with ether, 250 cc. of absolute ether and 17 grams of pure ethyl malonate¹ were added and the mixture boiled with an upright condenser, for some hours, till the conversion of the malonic ester to the sodium salt seemed complete, 18.8 grams of trimethylparaconyl chloride were added and the mixture boiled again for 8 hours and allowed to stand over night. On adding dilute hydrochloric acid, about 6 grams of a substance remained, which was nearly insoluble in ether. This proved to be *ethyl ditrimethylparaconylmalonate*,



It is deposited from alcohol in small, compact crystals, which melt at 162°–163°. Analysis:

	Calculated for C ₂₃ H ₃₂ O ₇ .	I.	Found. II.	III.
C	59.05	57.64	58.09	58.77
H	6.84	6.66	6.73	. .

By distilling the residue from the ethereal solution, there were obtained 12.5 grams of an oil, which boiled at 250°–255° (60 mm.). This was ethyl trimethylparaconylmalonate. An

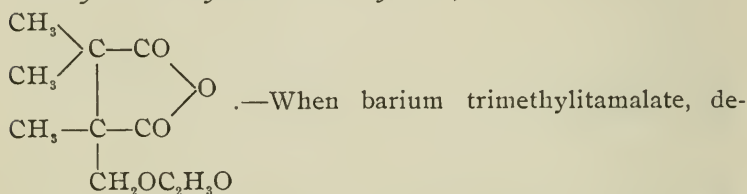
¹ See J. Am. Chem. Soc., 23, 397.

alcoholic solution of it gives a deep red color with ferric chloride. It is soluble in dilute sodium hydroxide solution, while a more concentrated one converts it into a difficultly soluble sodium salt. Analysis:

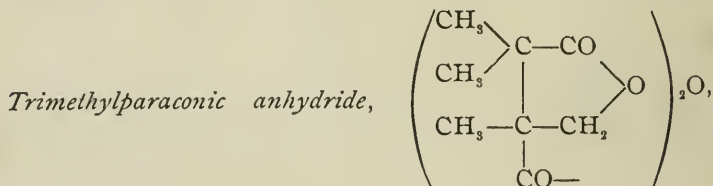
	Calculated for $C_{15}H_{22}O_7$.	I.	Found. II.
C	57.32	57.11	56.33
H	7.01	6.87	7.02

Attempts to reduce the ester, by shaking it with water and with 3 per cent sodium amalgam, appeared to be partially successful, but definite reduction-products were not secured.

Acetyl Trimethylitamalic Anhydride,



scribed on p. 360, is boiled for half an hour with acetic anhydride, there is formed trimethylparaconic anhydride and acetyl trimethylitamalic anhydride. Sixty grams of the barium salt gave about 27 grams of the anhydride and 12.5 grams of its acetyl derivative. By means of a Gooch crucible, with a disk of hardened filter-paper, the solution of these substances in acetic anhydride was filtered from the barium acetate. The acetic anhydride was distilled under diminished pressure and some dry ether was added to the residue. This caused the anhydride, which is nearly insoluble in ether, to separate slowly. A little acetic anhydride was added to the ethereal mother-liquors and, after distilling away the ether, the residue was distilled under diminished pressure, giving the acetyl derivative.



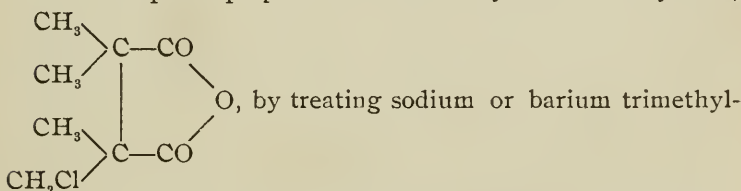
separates in small, granular crystals, which melt at 154° – 155° . The compound may also be obtained by boiling trimethylparaconic acid with acetic anhydride. Analysis :

	Calculated for $C_{16}H_{22}O_7$.	I.	Found. II.
C	58.86	58.24	59.30
H	6.80	6.91	6.92

Acetyl trimethylitamic anhydride, obtained as described above, is an oil which boils at 185° – 195° (20 mm.). Analysis:

	Calculated for $C_{10}H_{14}O_5$.	I.	Found. II.
C	56.05	55.55	56.02
H	6.59	6.73	6.71

An attempt to prepare chlortetramethylsuccinic anhydride,



paraconate with phosphorus pentachloride was not successful.

The study of the acetyl derivative and an attempt to effect the desired synthesis with its aid will be continued.

JOHNS HOPKINS UNIVERSITY.
June, 1904.

Contributions from the Sheffield Laboratory of Yale University.

CXXI.—SYNTHESIS OF IODGORGIC ACID.

BY HENRY L. WHEELER AND GEORGE S. JAMIESON.

The name gorgonin was applied by Drechsel¹ to the dark-brown, horn-like substance, containing as much as 7.89 per cent of iodine,² composing the axial skeleton of the Mediterranean coral *Gorgonia Cavolinii*.

When this albuminoid or keratin was hydrolyzed by barium hydroxide, a small amount of a crystalline substance, contain-

¹ Z. f. Biologie, **33**, 90 (1896).

² In view of the work of Mendel, Am. Jour. Physiol., **4**, 243 (1900), and Cook, *Ibid.*, **12**, 95 (1904), this content of iodine is much higher than that of other Gorgonian corals.

ing iodine, was obtained. It was named "jodgorgosäure" and was supposed, by Drechsel, to be an iodaminobutyric acid. It is the only crystalline, iodine cleavage product that has been obtained, either from a natural or an artificial iodoprotein and it is noteworthy that the decomposition of gorgonin with baryta water takes place with far greater ease than in the case of other proteins.

Henze¹ has recently made a more thorough study of gorgonin and its decomposition-products by acids and barium hydroxide. He not only isolated the iodogorgoic acid, but also examined its properties.²

From the work of the above investigators we know that this acid is precipitated from neutral solutions by the addition of silver nitrate, the gray or white silver salt being readily soluble in dilute nitric acid. When decomposed by hydrogen sulphide it gives the acid, which is deposited from water in long, lancet- (Henze) or whetstone-shaped (Drechsel), yellowish-white crystals. It is sparingly soluble in water and melts at 205° with decomposition. It dissolves readily in alkalis and sodium carbonate and is precipitated by neutralizing with acids. Dilute mineral acids give salts, strong nitric or sulphuric acids liberate iodine.

Henze made the important observation that the substance gives the xanthoprotein reaction and therefore the acid is an aromatic derivative and not an iodaminobutyric acid. It does not give Millon's reaction, but Henze states that this by no means excludes the possibility that iodogorgoic acid is a tyrosine derivative, as Blum and Vaubel³ found that the test does not apply to phenolic derivatives with substituents in the ortho or meta positions to a hydroxyl group. The quantity of material at Henze's disposal was so small, that nothing further could be done with the acid than to make a nitrogen and an iodine determination. He states the analytical results serve to confirm the fact that the substance cannot be an iodamino-

¹ Z. physiol. Chem., **38**, 60 (1903).

² In addition to this iodamino acid, the work of Drechsel and Henze has shown that the following iodine-free cleavage-products can be isolated, or identified as being present in gorgonin: Leucine, tyrosine, lysine, lysatiuine?, histidine, arginine, phenylalanine?, glycolic and an unidentified acid containing chlorine.

³ J. prakt. Chem., **57**, 365 (1898).

butyric acid and adds, that it would be useless to derive a formula from them.

When proteids are acted on by halogens, the products no longer respond to Millon's test, indicating that probably the tyrosine group is attacked.¹ Oswald believes his experiments show that iodine enters entirely, or for the most part, the aromatic groups.²

He examined the action of excess of iodine on tyrosine, using the method usually employed to introduce the halogen into proteids, *i. e.*, in sodium bicarbonate solution, at 45°. The resulting liquid failed to respond to Millon's test. The iod-acid he obtained formed a syrup, that refused to crystallize, even after many weeks. In a desiccator it dried to an amorphous mass, which contained 63.18 per cent of iodine. He therefore concluded that this substance was a triiodtyrosine, which requires 64.97 per cent of iodine. Obviously this was not iodgorgoic acid.

We have found that a diiodtyrosine, having all the properties of iodgorgoic acid, can be prepared by adding a little less than the calculated amount of iodine to solution of *L*-tyrosine, in two molecular proportions of potassium or sodium hydroxide, at ordinary temperatures.

There are now several methods for the synthesis of racemic tyrosine³ and this has been separated into its active components by Emil Fischer.⁴ The complete synthesis of iodgorgoic acid can, therefore, be considered as having been effected.

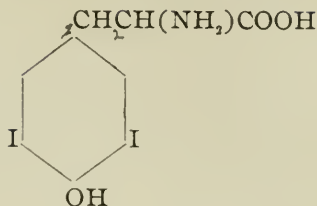
It gives a di-silver salt, therefore the hydroxyl hydrogen is not replaced by iodine. The fact that halogens attack phenols in the ortho and not the meta position to the hydroxyl and that the acid does not give Millon's reaction, leads to its formulation as 3,5-diiodtyrosin :

¹ Hofmeister : Z. physiol. Chem., **24**, 159 (1898). Blum and Vaubel : *Loc. cit.*

² Beitrage chem. Physiologie, **3**, 413, 521 (1903).

³ Erlenmeyer, Lipp : Ann. Chem. (Liebig), **219**, 170 (1883). Erlenmeyer jun., Halsey : Ber. d. chem. Ges., **30**, 2981 (1897). Ann. Chem. (Liebig), **307**, 142 (1899).

⁴ Ber. d. chem. Ges., **32**, 3641 (1899).



In this paper we give a description of the preparation and properties of iodogorgoic acid and a description of some of its immediate derivatives. We hope, later, to prove definitely the position of iodine in the compound.

EXPERIMENTAL.

Diiodtyrosine, $\text{C}_9\text{H}_9\text{O}_5\text{NI}_2$.—The tyrosine employed by us was prepared from silk, horn and casein. It was dissolved in ammonia, precipitated by acetic acid and crystallized from water. It melted at about 295° .

Three grams of tyrosine were dissolved in water (50 cc.), containing potassium hydroxide (2 grams). To this solution 7.9 grams of finely pulverized iodine were added, in small portions, with vigorous shaking. The reaction began at once and, after several additions of iodine had been made, the diiodtyrosine separated as a light-brown, crystalline precipitate. This was boiled with 100 cc. of water and filtered hot from about 0.5 gram of amorphous, brown resin. The pale-yellow filtrate deposited radiating bunches of needle-like prisms, which were usually pale-pink. Another crystallization from water gave colorless crystals of pure diiodtyrosine, melting, with sudden decomposition and violent effervescence, at 196° – 205° , according to the rate of heating, the amount of material used, etc. Henze states that iodogorgoic acid melts at 205° with decomposition. The average yield of pure material was 3.5 grams, from 3 grams of tyrosine, or 48 per cent of the calculated. The by-products being the above resinous substance, containing 55 per cent of iodine and some more soluble material which, on evaporating the aqueous solution, gave more of the resinous substance. Analysis :

	Calculated for $C_9H_9O_3NI_2$.	Found.
N	3.23	3.24
I	58.66	58.43 ¹

Henze states that iodorgoic acid is very sparingly soluble in water. We find that our diiodtyrosine dissolves fairly readily in hot water and sparingly in cold. One hundred parts of water, at 25°, dissolved 0.2 gram substance. The aqueous solution is acid to litmus. Diiodtyrosine dissolves to only a slight extent in alcohol and it is insoluble in benzene and chloroform. It dissolves readily in ammonium hydroxide and the alkalis. Dilute mineral acids form salts, strong nitric and concentrated sulphuric acid liberate iodine. When diiodtyrosine is warmed with hydriodic acid it is quantitatively converted into tyrosine. Zinc and hydrochloric acid (nascent hydrogen) also give tyrosine. Prolonged boiling with baryta water only partially decomposes the acid, but it is more readily decomposed with alkali. It forms sparingly soluble salts with silver, lead and copper and is precipitated from aqueous solutions by phosphotungstic acid and mercurous nitrate. Platinum chloride, mercuric chloride and picric acid give no precipitates. With superheated steam it forms a resin free from iodine. It responds to the xanthoprotein test, but not to Milon's reaction.

Action of Water.—Diiodtyrosine can be repeatedly crystallized from water without change. One-half gram was heated in a closed tube, with 5 cc. of water, for 2 hours, at 120°–130°; only a partial decomposition took place. On heating 2 hours longer, at about 155°, the material was converted into a brown, insoluble, amorphous resin, the iodine being converted into hydriodic acid.

Action of Barium Hydroxide.—Diiodtyrosine (0.5 gram) was boiled for 2 hours with barium hydroxide (12 grams) and water (50 cc.). The barium from 5 cc. of this solution was precipitated by means of carbon dioxide, silver nitrate added and the resulting precipitate treated with dilute nitric acid, free from

¹ The iodine determinations given in this paper were made by evaporating the substance to dryness with strong nitric acid and silver nitrate, etc. When checked by a Carius determination the results agreed.

nitrous acid, whereupon it dissolved completely. It follows, therefore, that no iodine had been removed by this treatment and that the material remained unaltered.

The remainder of the baryta solution was boiled for 30 hours, about 10 per cent of the iodine in the diiodtyrosine was liberated.

Action of Hydriodic Acid.—Diiodtyrosine (0.5 gram) was boiled with 5 cc. of strong hydriodic acid, for a few minutes, then evaporated to dryness on the water-bath. The black residue was dissolved in a little water and decolorized by sodium bisulphite. Careful addition of ammonia yielded tyrosine (0.2 gram), m. p. about 294° .

Diiodtyrosine Hydrochloride.—Diiodtyrosine (0.5 gram) was evaporated with 20 cc. of dilute hydrochloric acid to about 5 cc. On cooling, radiating bunches of colorless needles separated; these were pressed on paper and dried over potassium hydroxide for analysis:

	Calculated for $C_9H_9O_3NI_2.HCl$.	Found.
Cl	7.56	7.56

Drechsel states that the hydrochloride of iodogorgoic acid is decomposed by water with separation of crystals of the free acid. Henze says that he could not confirm this observation, although he brings no analytical data to support his statement.

The hydrochloride, obtained as described above, was recrystallized from a small amount of water; the product contained only 1.4 per cent of chlorine; the salt is, therefore, decomposed by water.

The *sulphate* was obtained by dissolving the diiod acid in dilute sulphuric acid. It formed colorless, slender prisms which were very soluble in water. Analysis:

	Calculated for $C_9H_9O_3NI_2.H_2SO_4$.	Found.
H_2SO_4	18.49	18.74

Silver Salt of Diiodtyrosine.—When aqueous solutions of silver nitrate and diiodtyrosine are mixed, a white, flocculent precipitate separates at once; the amount can be increased by

the addition of a few drops of ammonia. The precipitate, dried at about 50°–60°, remained white.

	Calculated for $C_9H_7O_3NI_2Ag_2$.	Found.
Ag	33.38	33.49

The salt is readily soluble in pure, dilute nitric acid and is reprecipitated by neutralization with ammonia. Strong nitric acid readily separates silver iodide, especially on warming. It is soluble in excess of ammonia.

The *copper salt* was obtained, in a similar manner, from copper sulphate and separated immediately as a flocculent, amorphous, pale-blue precipitate, insoluble in water. It was dried at 120° (Analysis I.). A salt of the same appearance was formed on adding copper hydroxide to warm, aqueous solution of the acid and then treating the precipitate with acetic acid and water. This was dried at 100° (Analysis II.).

	Calculated for $(C_9H_5O_3NI_2)_2Cu$.	I.	Found.	II.
Cu	6.85	6.74		6.76

A salt, of the same appearance as the above, is also formed on adding solution of copper acetate to cold solution of diiodtyrosine; the pale-blue precipitate, in this case, was dried over sulphuric acid, during 5 days. The water was determined at 120°–125°.

	Calculated for $(C_9H_5O_3NI_2)_2Cu.H_2O$.	Found.
H ₂ O	1.90	1.77

A *lead salt* is precipitated as a white, or cream-colored, apparently amorphous powder on mixing solutions of lead acetate and diiodtyrosine.

Monoacetyldiiodtyrosine was obtained when diiodtyrosine (1 gram) was boiled with excess of acetic anhydride. The acid dissolved and in a few minutes the acetyl compound separated. It was powdered and purified by boiling with alcohol and water. It is insoluble in water and amyl acetate, very sparingly soluble in alcohol and formed a pale-yellow powder, which effervesced at about 225°.

	Calculated for $C_{11}H_{11}O_4NI_2$.	Found.
I	53.47	53.24

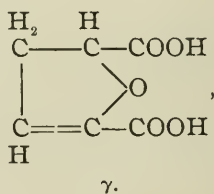
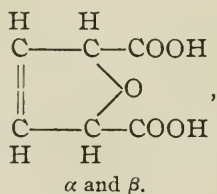
NEW HAVEN, CONN.,
Dec. 14, 1904.

Contributions from the Chemical Laboratory of Harvard College.
ON THE OPTICALLY ACTIVE ISOMERS OF THE
 β -DIHYDROFURFURAN- α,α' -DICARBOXYLIC
ACID.¹

BY H. B. HILL AND F. W. RUSSE.

The principal object of the work described in this paper was the separation of the β -dihydrofurfuran- α,α' -dicarboxylic acid into its optical isomers, which had not yet been obtained in a state of purity and the study of the properties of these two bodies.

The β -dihydrofurfuran- α,α' -dicarboxylic acid (dihydrodehydromucic acid) was discovered by Fittig and Heinzelmann,² in 1876. Seelig,³ in 1879, separated the product of the reduction into two isomeric acids, the existence of which was denied by Schrötter,⁴ in 1888, but in 1901 A. S. Wheeler and one of us⁵ showed, not only that Seelig's α - and β -acids existed, but that there was also a third (γ) acid contained in this product. The formulas of these three acids were also established, in that paper, as



and the α -acid was shown to be the inactive, the β -acid the racemic form.

¹ Most of the experimental work described was done under the direction of Professor H. B. Hill, but it was finished and the paper written after his lamented death.

C. L. J.

² Ber. d. chem. Ges., 9, 1199.

³ *Ibid.*, 12, 1085.

⁴ Sitzun. Wien., 97, 2 b, 409.

⁵ THIS JOURNAL, 25, 463; also Hill: *Ibid.*, 25, 439.

In taking up the work again we found that the cinchonine salt of the laevo- β -acid is much less soluble than that of the dextro- β -acid; accordingly, by five crystallizations of this salt from water, we have succeeded in preparing the salt of the pure laevo- β -acid. The mother-liquors from the first crystallization of the laevo cinchonine salt contained most of the dextro acid, which was set free and converted into the strychnine salt, as it had been found that the dextro salt of this alkaloid was somewhat less soluble than the laevo salt. By repeated crystallizations from water the strychnine salt of the dextro acid was obtained pure.

The two optically active acids resemble each other in the closest way, but differ strikingly from the racemic acid in many respects, as is shown by the following comparison. All three crystallize well from water, with $1\text{H}_2\text{O}$, and give crystals of the anhydrous acid from ether, all of which are alike in general appearance, so that they could be distinguished, if at all, only by a crystallographic study. The anhydrous racemic acid melts at $178^\circ\text{--}179^\circ$ (cor.), the dextro and laevo acids at 144° (uncor.). The latter seem to be more soluble in water or ether than the racemic form. The three barium salts crystallize with $1\frac{1}{2}\text{H}_2\text{O}$, but the salts of the optically active acids seem to be more soluble than that of the racemic acid. The lead salt of the racemic acid crystallizes with $1\text{H}_2\text{O}$, only half of which is given off at 195° ; the lead salt of the dextro or laevo acid crystallizes with $2\text{H}_2\text{O}$, all of which goes off at 135° . The optically active lead salts are about fifty times as soluble as that of the racemic acid.

We have tried also to separate the γ -dihydrofurfuran- α,α' -dicarboxylic acid into two optically active isomers, but encountered great difficulties because of the tendency of the acid (or its alkaloid salts) to be converted, by boiling with water, into a jelly from which the original acid could not be obtained again by any means that we have been able to find. This jelly contains $2\text{H}_2\text{O}$ more than the γ -acid and, like that, is a dibasic acid. A similar conversion of the β -acid to a jelly was also observed. We can report only the probable existence of optical isomers of the γ -acid. Several of its salts are described.

EXPERIMENTAL.

Preparation of β -Dihydrofurfuran- α,α' -dicarboxylic Acid, $C_4H_4O(COOH)_2$.—The acid for our work was prepared by the following method: Ten grams of dehydromucic acid were suspended in 100 cc. of water and brought into solution by the addition of solid sodic hydrate; 300 grams of 3 per cent sodium amalgam were then added and the mixture was allowed to stand at ordinary temperatures until a drop gave no precipitate of dehydromucic acid on the addition of hydrochloric acid, which usually occurred in four hours. The liquid was then decanted from the mercury, boiled for 1 minute, allowed to cool, made slightly acid with nitric acid, filtered to remove any dehydromucic acid which had escaped reduction, neutralized with sodic hydrate and mixed with 106 grams of plumbic nitrate dissolved in water. On standing for 2 days the nearly insoluble lead salt of the β -acid had separated in crystals; these were filtered out and treated with boiling water, until all of the more soluble lead salt of the α -acid had been dissolved. They were then suspended in water and strongly acidified with hydrochloric acid, after standing over night the plumbic chloride was filtered out and the filtrate treated with ether, in a continuous extractor. The ether extract left, on evaporation, the pure crystalline β -acid. Yield, 1–1.5 grams.

This method of preparation differs in some important respects from that previously given by A. S. Wheeler and one of us.¹ Common sodium amalgam is used instead of the specially prepared, pure and finely divided amalgam recommended there. The yield, to be sure, is not so good with this ordinary preparation, but the loss is more than compensated for by the saving of time in the manufacture of the amalgam.

A more important difference between our process and the older one has for its object the avoidance of a gummy substance, which frequently replaced the crystalline acid, in part, or, in extreme cases, completely. Some preliminary experiments showed that the crystalline acid was converted into this gum during the heating of the reduced liquid, poured off from the mercury. The progress of this change was studied in the

¹ THIS JOURNAL, 25, 463, 439.

series of experiments recorded in the following table. In this work the specially prepared granular sodium amalgam was used.

Temperature during reduction.	Length of boiling.	Yield of lead salt.	State of free acid.	Per cent of crystalline acid.
		Per cent.		
20°-40°	15 min.	75	Jelly	None
"	15 "	59.6	"	"
"	5 "	46.8	" part crystalline	
24°	2 "	58	Crystalline with some gum	57
"	2 "	47	" " " "	42
23°-30°	Just to boiling	38	"	31
18°-24°	Just to boiling	32	"	27
"	Just to boiling	42	"	31

From these results it appears that the amount of jelly formed depends on the length of the boiling and that the solution should never be boiled more than 2 minutes, but, on the other hand, the best yield is not obtained if the heating is stopped as soon as the solution begins to boil. We have, therefore, adopted 1 minute as the length of boiling, which gives the best result, in place of the boiling for a few minutes recommended in the earlier process. We are able to give no account of the nature of this gum, but it is probably closely related to the gummy derivative of the γ -acid, discussed later in this paper.

The older method of decomposing the lead salt with sulphuretted hydrogen is not only less convenient than our method with hydrochloric acid and ether, but has the additional disadvantage of giving a product contaminated with sulphur, if any of the gummy impurity is present. The hydrochloric acid process was also found to be more convenient than one in which the lead was removed by treatment with sodic carbonate. The only remaining difference between the

two processes consists in our use of sodic hydrate, instead of sodic carbonate, to dissolve the dehydromucic acid.

Separation of the β -Dihydro-furfuran- α,α' -dicarboxylic Acid into its Optical Isomers—The cinchonine and strychnine salts of the β -acid crystallize well and were, therefore, selected for further study. Upon crystallizing the cinchonine salt from water and examining with polarized light the acids derived from the fractions, it was found that the less soluble portion of the salt contained the laevo acid, the more soluble portion the dextro acid and further, that the difference in solubility of these two salts is considerable, the salt of the dextro acid being more than twice as soluble as that of the laevo acid. On the other hand, we found that the strychnine salt of the laevo acid is about one and one-half times as soluble as that of the dextro acid.

The method of separation, founded on these observations, was as follows: Cinchonine was added, in excess, to a hot aqueous solution of the β -dihydrofurfuran- α,α' -dicarboxylic acid of such a concentration that the resulting solution of the cinchonine salt would be saturated at the boiling-point. The excess of cinchonine was filtered out through a steam-filter and the solution allowed to cool. The crystals thus obtained were recrystallized from boiling water, until polariscope tests showed that the pure laevo salt had been obtained, which usually needed four recrystallizations. The progress of the purification was much delayed by the deposition of the more soluble alkaloid salt from the solution, which had crawled above the surface of the liquid. This difficulty was entirely removed by the simple device of putting the beaker containing the hot solution of the salts into a crystallizing pan partly filled with hot water, a large beaker was then inverted over the smaller one and, as this was sealed by immersion in the liquid in the pan, the crystallization took place in an atmosphere saturated with the vapor of water so that there was no evaporation of the mother-liquor drawn upon the sides of the beaker. The apparatus should be so arranged that the inner beaker may not be upset by the rise of water in the larger one during cooling.

The dextro acid was prepared from the mother-liquors of the first crystals of the cinchonine salt. For this purpose hydrochloric acid was added to them until a reaction was obtained with logwood paper and the acidified liquid was then extracted with ether. The crude dextro acid, thus obtained, was treated, in hot aqueous solution, with an excess of strychnine and the strychnine salt recrystallized from hot water till pure, the purity being determined, as with the laevo acid, by the constancy of the rotary power of the free acid. That the two acids were pure was further shown by the fact that their rotary powers were equal and opposite.

Seventeen grams of the *β*-acid yielded, by this treatment, 3 grams of laevo and 3 grams of dextro acid.

Cinchonine Salts of the Dextro and Laevo β-dihydrofurfuran-α,α'-dicarboxylic Acids.—The salt of the laevo acid crystallizes from water in silky, slightly brownish-white needles, arranged in radiating groups. It is less than half as soluble as the dextro salt and is slightly decomposed, with separation of cinchonine, when dissolved in water.

The salt of the dextro acid is deposited from solutions in a white crystalline crust, apparently made up of needles. It is very soluble in water. The salts of both acids dissolve in ethyl or methyl alcohol, or in chloroform, but are insoluble in ether, benzol, acetone, or ligroin.

Strychnine Salts.—The salt of the dextro acid crystallizes in white, silky needles, usually, but not always, arranged in radiating groups. It is less soluble in water than the laevo salt, but the difference in solubility (about $1\frac{1}{2}$ times) is much less than that between the cinchonine salts. The laevo salt forms white, silky needles, similar to those of the dextro salt. Both are soluble in ethyl or methyl alcohol or in chloroform, but insoluble in ether, benzol, ethyl acetate, acetone, or ligroin.

Dextro-β-dihydrofurfuran-α,α'-dicarboxylic Acid,
 $C_4H_4O(COOH)_2 \cdot H_2O$.—This acid was obtained from the strychnine salt by adding hydrochloric acid, until the solution gave a test with logwood-paper, filtering out any chlorhydrate of strychnine that was precipitated and extracting with ether.

It was dried in the air and tested for water of crystallization.
0.3581 gram air-dried substance lost 0.0384 gram at 100°.

	Calculated for $C_4H_4O(COOH)_2 \cdot H_2O$.	Found.
H_2O	10.23	10.73

As the method of preparation from the racemic β -acid leaves no doubt in regard to its composition, no other analyses of the free acid were made.

Properties of the Dextro Acid.—It crystallizes from ether in thick, anhydrous prisms, from water in thick, transparent, white plates, which contain $1H_2O$ and collapse at about 100°. The anhydrous acid melts at 144°. It is freely soluble in water or ethyl alcohol, sparingly in ether, but more soluble than the racemic β -acid, especially if the ether is hot; insoluble in benzol, chloroform, or ligroin. It can be crystallized from ether or from ether and ligroin. Some of its salts are described later in the paper and its behavior toward polarized light will be considered after the description of the laevo acid.

Laevo- β -dihydrofurfuran- α, α' -dicarboxylic Acid,
 $C_4H_4O(COOH)_2 \cdot H_2O$.—This acid was obtained from the cinchonine salt by acidifying the solution with hydrochloric acid, until it gave a test with logwood-paper and extracting with ether.

- I. 0.1141 gram air-dried substance lost 0.0122 gram at 100°.
II. 0.1383 gram substance lost 0.0145 gram at 100°.

	Calculated for $C_4H_4O(COOH)_2 \cdot H_2O$.	I.	Found.	II.
H_2O	10.23	10.64		10.48

Properties of the Laevo Acid.—It resembles the dextro and the racemic acid most closely, both in the crystals containing $1H_2O$ and the anhydrous crystals obtained from ether and ligroin. It melts at 144°, when anhydrous, like the dextro acid and shows the same solubilities in the common solvents.

Specific Rotary Power of the Dextro and Laevo Acids.—The acids for these experiments were prepared from the purest specimens, made as described above, by recrystallizing these once from water, driving off the water of crystallization at

100° and extracting the dried substance with ether, discarding the first and last portions of the extract. Finally it was dried at 100° to constant weight. The solutions were prepared at 20° and the room in which the readings were made varied but little from this temperature. The sodium flame was used.

Dextro Acid.

<i>c.</i>	α .	λ .	$[\alpha]_D$.
10.15	+48°.78	1 dm.	+480.7
5.08	24°.67	1 "	485.4
2.525	12°.35	1 "	489.2
0.629	6°.31	2 dms.	502.0
0.157	1°.63	2 "	519.0
1.160	5°.75	1 dm.	496.0
0.582	2°.92	1 "	502.0

Laevo Acid.

<i>c.</i>	α .	λ .	$[\alpha]_D$.
10.04	-48°.04	1 dm.	-478.7
5.01	24°.22	1 "	483.4
2.517	12°.29	1 "	488.3
0.627	6°.35	2 dms.	507.0
0.158	1°.67	2 "	533.0

In these tables column *c* gives the concentration in grams for 100 cc. of solution; α the angle read; λ the length of the tube; and $[\alpha]_D$ the specific rotary power. The last two determinations of the dextro acid were made with a different sample.

These results show that the specific rotary power increases slightly with the dilution. The differences between the determinations for the dextro and laevo acids amount to about 0.5 per cent, with the less dilute solutions, but with the most dilute it rises to 2.6 per cent, which is undoubtedly due to the smallness of the angle read in these cases.

To make certain that no serious error was introduced into the determinations by slight changes of temperature during the readings, two readings were made with the same specimen of the dextro acid, the one at 16°.5 gave a rotation angle of 9°.90, the other, at 24°.5, gave an angle of 9°.87. These differences are no greater than the error of reading of the instrument and, as any accidental variations of temperature during the determinations must have been smaller than the difference between these two experiments, the temperature could have had no appreciable influence on our results.

Salts of the β -Acid.

Baric Dextro- β -dihydrofurfuran- α,α' -dicarboxylate,
 $C_4H_4O(COO)_2Ba \cdot 1\frac{1}{2}H_2O$.—The salt was made by boiling a solu-

tion of the dextro acid with excess of baric carbonate, until the liquid was neutral. The remaining carbonate was then filtered out and the filtrate concentrated, when the barium salt crystallized out. It was dried in the air. Analysis:

0.3345 gram of the air-dried salt lost 0.0293 gram at 105° .

	Calculated for $C_4H_4O(COO)_2Ba\frac{1}{2}H_2O$.	Found.
H_2O	8.43	8.76

0.3045 gram of the salt gave, on evaporation with sulphuric acid, 0.2407 gram $BaSO_4$.

	Calculated for $C_4H_4O(COO)_2Ba$.	Found.
Ba	46.83	46.51

It forms small, white crystals, which dissolve in about 50 parts of water, the solubility increases only slightly with increase of temperature. It loses its water of crystallization *in vacuo*. The racemic salt also crystallizes with $1\frac{1}{2} H_2O$.

Baric Laevo- β -dihydrofurfuran- α, α' -dicarboxylate
 $C_4H_4O(COO)_2Ba.1\frac{1}{2}H_2O$.—This salt was prepared in the same way as the dextro compound. Analysis:

I. 0.3998 gram of air-dried salt lost 0.0355 gram at 105° .

II. 0.7137 gram lost 0.0667 gram.

	Calculated for $C_4H_4O(COO)_2Ba1\frac{1}{2}H_2O$.	I. Found.	II.
H_2O	8.43	8.88	9.35

The sample used in II. was obtained by the spontaneous evaporation of the aqueous solution, that used in I was evaporated by heat.

0.3634 gram of the salt, dried at 105° , gave 0.2892 gram of $BaSO_4$.

	Calculated for $C_4H_4O(COO)_2Ba$.	Found.
Ba	46.83	46.82

The salt resembles the corresponding dextro compound most closely in appearance and other properties.

Plumbic Dextro- β -dihydrofurfuran- α, α' -dicarboxylate,
 $C_4H_4O(COO)_2Pb.2H_2O$.—The salt was prepared by boiling an

aqueous solution of the acid with plumbic carbonate and filtering off the excess of the latter. Upon cooling, crystals of the salt separated in small amount; a larger quantity was obtained by allowing the solution to evaporate spontaneously, or concentrating it by heat; in each case the salt with $2\text{H}_2\text{O}$ was obtained. It was purified by recrystallization from water.

I. 0.2835 gram of the air-dried salt lost 0.0247 gram *in vacuo* and only 0.0044 gram, in addition, at 135° .

II. 0.3339 gram lost 0.0294 at 135° .

	Calculated for $\text{C}_4\text{H}_4\text{O}(\text{COO})_2\text{Pb}_2\text{H}_2\text{O}$.	Found <i>in vacuo</i> .
$2\text{H}_2\text{O}$	9.02	8.72
		Found at 135° .
		I. II.
$2\text{H}_2\text{O}$	9.02	10.26 8.80

The salt, therefore, contains $2\text{H}_2\text{O}$, which it loses *in vacuo*. If heated at 180° , it was decomposed, as it took on a pale yellow color and gave percentages of lead which did not correspond to those calculated from the formula.

0.2543 gram of the salt, dried at 135° , gave 0.2128 gram of PbSO_4 .

	Calculated for $\text{C}_4\text{H}_4\text{O}(\text{COO})_2\text{Pb}$.	Found.
Pb	57.01	57.15

Plumbic Laevo- β -dihydrofurfuran- α, α' -dicarboxylate, $\text{C}_4\text{H}_4\text{O}(\text{COO})_2\text{Pb} \cdot 2\text{H}_2\text{O}$.—This was prepared in the same way as the dextro salt, which it resembles most closely in properties.

I. 0.3805 gram of the air-dried salt lost 0.0369 gram at 135° .

II. 0.4422 gram lost 0.0405 gram.

	Calculated for $\text{C}_4\text{H}_4\text{O}(\text{COO})_2\text{Pb}_2\text{H}_2\text{O}$.	I.	Found. II.
$2\text{H}_2\text{O}$	9.02	9.70	9.16

0.3431 gram of the salt, dried at 135° , gave 0.2861 gram PbSO_4 .

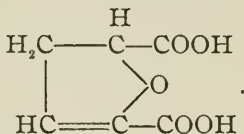
	Calculated for $\text{C}_4\text{H}_4\text{O}(\text{COO})_2\text{Pb}$.	Found.
Pb	57.01	56.97

Some determinations of the solubilities of the dextro and laevo lead salts gave unsatisfactory results, apparently because they form saturated solutions only with great difficulty. These

experiments indicate, however, that the two have essentially the same solubility, which is about fifty times as great as that of the racemic salt. If saturated solutions of the dextro and laevo salts are mixed and the sides of the vessel scratched with a glass rod, the racemic salt crystallizes out at once.

γ -Dihydrofurfuran- α,α' -dicarboxylic Acid.

This acid was discovered by A. S. Wheeler and one of us,¹ who proved that its structural formula is



In order to characterize it more thoroughly we have studied some of its salts and have tried to separate it into its optical isomers, but our work has not made such progress as we could wish, on account of the easy conversion of the acid or its salts with alkaloids into another substance, when heated in aqueous solution.

We have first to correct a mistake in regard to the melting-point of the γ -acid, which, owing to a misunderstanding, has found its way into the paper by Wheeler and one of us.² It is stated there that the acid decomposes, without melting, at 194° ; in reality it melts and almost immediately decomposes, with formation of bubbles, at temperatures between 175° and 190° , according to the rapidity of the heating. A number of specimens, purified by crystallization from different solvents, were tried, but no constant melting-point could be obtained and it was shown by experiment that the variations depended on differences in the method of heating. As these melting-points averaged 180° , that is, 14° lower than the melting-point taken by Wheeler, we analyzed the substance so as to be sure that it was the γ -acid.

I. 0.2049 gram substance gave, on combustion, 0.3451 gram CO_2 and 0.0711 gram H_2O .

¹ THIS JOURNAL, 25, 439, 480.

² *Ibid.*, 25, 439, 480.

II. 0.2026 gram substance gave 0.3388 gram CO₂ and 0.0661 gram H₂O.

	Calculated for C ₄ H ₄ O(COOH) ₂ .	I.	Found.	II.
C	45.55	45.94		45.60
H	3.83	3.88		3.65

The alteration of the acid and its salts, already alluded to, was first observed in work with the alkaloid salts made for the purpose of separating the acid into its optical isomers. These, it was found, were frequently deposited from solutions as a jelly, which could not be made to crystallize. This jelly was formed most easily from aqueous solutions, but it was also obtained, with some difficulty, from solutions in alcohol or ether.

To study this subject more carefully, some of the γ -acid was dissolved in water and the solution evaporated to dryness on the steam-bath; the residue was a clear, slightly yellowish, viscous jelly. As this seemed to show that the jelly was formed by the action of heat, the following experiments were tried. A 10 per cent solution of the γ -acid was heated at 100° and at intervals a few drops were removed and allowed to cool on a watch-glass :

- | | | | |
|-----|-----------------|----------------------------------|-------------------------------|
| (1) | Cold, | good crystals of γ -acid. | |
| (2) | 5 minutes heat, | good crystals | |
| (3) | 10 " | " " " | } Very slight trace of jelly. |
| (4) | 15 " | " small " | |
| (5) | 20 " | " few " | |
| (6) | 25 " | " " " | slight amount of jelly. |
| (6) | 25 " | " " " | distinct " " " |
| (7) | 30 " | " jelly only. | |

As heating at 100° for 30 minutes was sufficient for complete conversion of the acid into the jelly, the effect of heating for 30 minutes, at other temperatures, was tried in the same manner. A 10 per cent solution of the acid was again used :

- (1) 40°, good crystals.
- (2) 50°, " "
- (3) 60°, " "
- (4) 70°, crystals beginning to be slightly coated with jelly.
- (5) 80°, distinct amount of jelly.
- (6) 90°, jelly.
- (7) 95°, "

The jelly does not lose weight after it is once evaporated to dryness on the water-bath, even if allowed to stand *in vacuo* for several weeks, nor does it show any signs of crystallization. If dissolved in the solvents used for recrystallizing the acid, it gives the jelly on evaporation, whether spontaneously or by heat. Its composition is constant, as shown by the following determinations, which were made by heating the weighed portions of the γ -acid for 2 hours, in aqueous solution, on the steam-bath and then evaporating off the water on the steam-bath and drying *in vacuo*.

I. 0.4264 gram acid gave 0.5238 gram jelly.

II. 0.8850 gram acid gave 1.0858 grams jelly.

	Calculated for $C_6H_6O_5 \cdot 2H_2O$.	I.	Found.	II.
Gain $2H_2O$	18.57	18.60		18.49

It is evident, therefore, that the γ -acid takes up $2H_2O$ in passing into the jelly. The γ -acid itself crystallizes without water, as was determined by Wheeler and one of us and confirmed by our own experiments. The jelly, prepared in determination I., was titrated with N/10 sodic hydrate solution and required 52.93 cc. The weight of γ -acid used in I. required 52.80 cc., so that the acidity is not effected by conversion of the acid into the jelly. A special experiment showed that no carbonic dioxide was given off during the formation of the jelly. Acetic anhydride, or benzoyl chloride had no action upon it and it was, apparently, inactive toward bromine, which acts on the γ -acid briskly.

Finally, the jelly could not be converted back into the crystalline acid by heating, standing *in vacuo*, boiling with acids, or alkalis, followed by extraction, or by attempts at crystallization from various solvents.

Salts of the γ -Acid.

Baric γ -Dihydrofurfuran- α, α' -dicarboxylate, $C_4H_4O(COO)_2Ba \cdot 2\frac{1}{2}H_2O$.—This salt was made by neutralizing a hot solution of the acid with a solution of baric hydrate. The salt, which separated on cooling, was recrystallized from water, pressed between filter-paper and dried to constant weight in the air, then *in vacuo* and finally at 160° .

0.8026 gram of air-dried salt lost 0.0711 gram at 160°.

	Calculated for $C_4H_4O(COO)_2Ba2\frac{1}{2}H_2O$.	Found.
$1\frac{1}{2}H_2O$	7.98	8.86

I. 0.1686 gram of the salt, dried at 160°, gave 0.1257 gram of $BaSO_4$.

II. 0.2661 gram salt, dried at 190°, gave 0.2031 gram $BaSO_4$.

	Calculated for $C_4H_4O(COO)_2BaH_2O$.	I.	Found.	II.
Ba	44.11	43.82		44.92

The salt used in II. had been dried at 190° and was somewhat decomposed, as indicated by its pale yellow color. These results show that the barium salt crystallizes with $2\frac{1}{2}H_2O$, one of which it retains even at 190°. It crystallizes in white, microscopic plates, which are somewhat soluble in cold water, freely so when heated.

Argentie γ-dihydrofurfuran-α,α'-dicarboxylate,
 $C_4H_4O(COOAg)_2 \cdot \frac{1}{2}H_2O$.—This was made by adding argentic nitrate to an aqueous solution of the neutral ammonium salt. It resembles the salt of the α-acid in that it contains $\frac{1}{2}H_2O$ which cannot be driven off without decomposition.

0.1742 gram of the salt gave 0.1717 gram of AgBr.

	Calculated for $C_4H_4O(COOAg)_2\frac{1}{2}H_2O$.	Found.
Ag	56.66	56.66

The salt crystallizes in small, white needles, which are sparingly soluble in cold water, much more so in hot.

Acid Potassic γ-Dihydrofurfuran-α,α'-dicarboxylate,
 $C_4H_4OCOOKCOOH$.—The salt was prepared by neutralizing a solution of the γ-acid with potassic hydrate and adding an equivalent amount of the acid. It separates in very fine, white crystals, which were recrystallized from water.

0.2875 gram of the air-dried salt gave 0.1266 gram of K_2SO_4 .

	Calculated for $C_4H_4OCOOKCOOH$.	Found.
K	19.95	19.77

The acid ammonium salt also can be obtained from its solutions in crystals, whereas we have not succeeded in obtaining crystals of the neutral ammonium or potassium salt. A white, insoluble lead salt was also made, but was not studied.

Attempts to Separate the γ -Acid into its Optical Isomers.—No conclusive results were obtained from this work, principally because of the difficulties introduced into it by the tendency of the acid, or its salts, to pass into a jelly, when heated in solution. We found it impossible to get crystals of the salts of the γ -acid with brucine, cinchonine, or morphine, but with strychnine, or quinine, crystalline salts were obtained. Fractional crystallization of these two, in most cases, led to products, which showed no rotation of the plane of polarized light, but, in one case, the strychnine salt gave a portion, which, after recrystallization, was dissolved in water, acidified with hydrochloric acid, filtered and the filtrate extracted with ether. Upon evaporating, a clear, pale yellow jelly was obtained, which, dissolved in water, gave a very minute, positive rotation of the plane of polarized light. We think it probable, therefore, that further work in this direction will lead to the isolation of optical isomers.

CAMBRIDGE, MASS.,
December 10, 1904.

DIPHENYLSULPHONEORTHOCARBOXYLIC ACID AND RELATED COMPOUNDS.¹

BY WILLIAM STONE WEEDON AND HOWARD WATERS DOUGHTY.

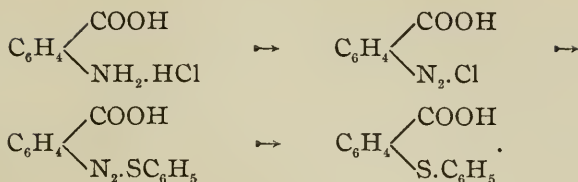
I. INTRODUCTION.

In 1890 Ziegler² prepared phenylthiosalicylic acid from anthranilic acid and thiophenol :

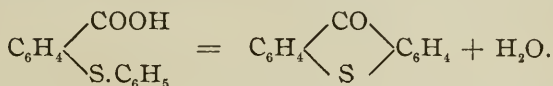
¹ The first portion of this investigation was carried out by Dr. Weedon, between February, 1901, and June, 1902. His conclusions were confirmed and the work extended by Dr. Doughty, January, 1903, to June, 1904. The results were separately submitted to the Board of University Studies, of Johns Hopkins University, in conformity with the requirements for the degree of Doctor of Philosophy, June, 1902, and June, 1904, respectively. For the sake of clearness and to avoid needless repetition, it was decided to combine the dissertations in one paper.

I. R.

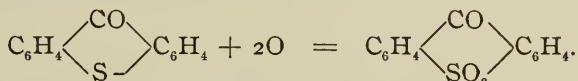
² Ber. d. chem. Ges., **23**, 2469.



He did not isolate the intermediate diazonium compound. By heating phenylthiosalicylic acid with concentrated sulphuric acid he obtained thioxanthone :

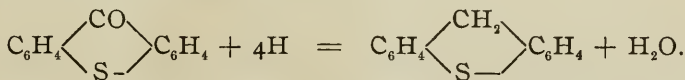


By the oxidation of thioxanthone, with chromic acid, he obtained benzophenonesulphone :



In 1891 Graebe and Schultess¹ continued the investigation of phenylthiosalicylic acid and its derivatives. They isolated the intermediate diazonium ether and then investigated the condensation-product, formed by heating phenylthiosalicylic acid with sulphuric acid, with the following results :

Thioxanthone, reduced by means of hydriodic acid or zinc dust, gives diphenylenemethane sulphide :



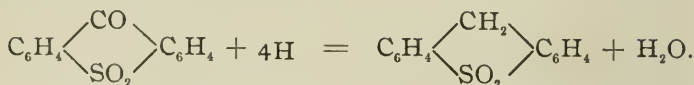
By the oxidation of this product benzophenonesulphone is formed ; the intermediate compounds were not isolated. They showed that this substance is identical with the one obtained by Beckmann,² as a by-product, when benzophenone was subjected to the action of fuming sulphuric acid.

When benzophenonesulphone is reduced by means of hydriodic acid, in the presence of red phosphorus, diphenylenemethanesulphone is formed, which is one of the two possible

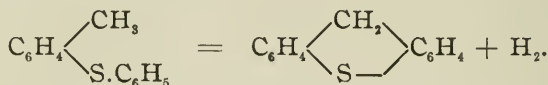
¹ Ann. Chem. (Liebig), 263, 1.

² Ber. d. chem. Ges., 6, 1112; 8, 992.

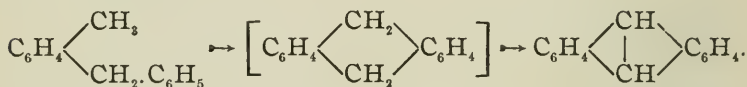
intermediate products between benzophenonesulphone and diphenylenemethane sulphide :



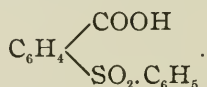
Graebe and Schultess also showed that orthodiazonium-toluene chloride yields orthotolylphenyl sulphide when treated with sodium thiophenolate. When the vapor of orthotolylphenyl sulphide is passed through a heated tube, diphenylenemethane sulphide is formed :



This is analogous to the formation of anthracene from ortho-benzyltoluene :



Graebe and Schultess also treated phenylthiosalicylic acid with dilute nitric acid and obtained a product to which they gave the name "sulphobenzideorthocarboxylic acid" and which they considered to have the formula



They analyzed the substance and obtained results in accord with this view. They did not describe any salts of the acid.

The corresponding acid in the para series, "paraphenylsulphonebenzoic acid," had already been made and described in 1878, by Michael and Adair,¹ who gave it this name and found its melting-point to be over 300°. They first prepared paratolylphenylsulphone from benzenesulphonic acid, toluene and phosphorus pentoxide and also from toluenesulphonic acid, benzene and phosphorus pentoxide. They oxidized this sulphone, by means of potassium permanganate, in

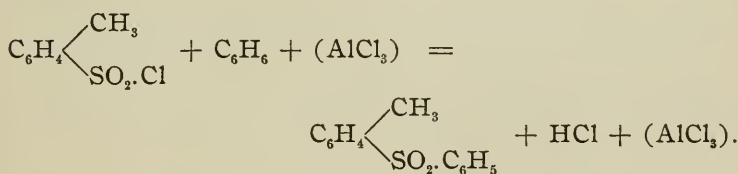
¹ Ber. d. chem. Ges., II, 116.

acetic acid solution and also in water and obtained a small yield of paraphenylsulphonebenzoic acid.

Paratolylphenylsulphone was also made in the same year, 1878, by Beckurts and R. Otto,¹ by the action of toluene and aluminum chloride on benzenesulphone chloride. In 1885 R. Otto² made it from toluenesulphone chloride, benzene and mercury diphenyl.

In 1895, Newell,³ working in this laboratory, made paraphenylsulphonebenzoic acid, by oxidizing paratolylphenylsulphone, which he obtained by the action of benzene and aluminum chloride on paratoluenesulphone chloride. He found the melting-point of paraphenylsulphonebenzoic acid to be 273° (uncor.), using a Zincke short-stemmed thermometer. He made various salts, the chloride, amide and anilide of the acid and, finally, by the action of the chloride on benzene and aluminum chloride, he obtained parabenzoyldiphenylsulphone.

In 1900, Canter,⁴ working in this laboratory, undertook the study of the analogous compounds in the ortho series. He used commercial orthotoluenesulphone chloride, from which as much of the para chloride as possible had been removed. This he treated with benzene and aluminum chloride and obtained a tolylphenylsulphone, which he supposed to be the ortho compound :



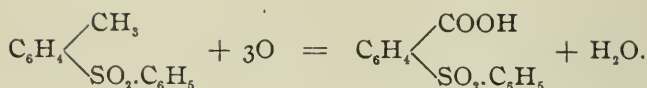
By oxidizing this sulphone with potassium permanganate, in water, he obtained an acid which should have the same formula as that assigned by Graebe and Schultess to the one prepared by them, by oxidizing phenylthiosalicylic acid with dilute nitric acid :

¹ Ber. d. chem. Ges., 11, 2068.

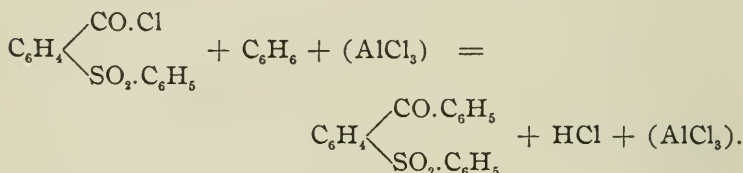
² *Ibid.*, 18, 249.

³ THIS JOURNAL, 20, 302.

⁴ *Ibid.*, 25, 96.



The acid obtained by Canter, which he called "orthophenylsulphonebenzoic acid," was distinctly different from the "sulphobenzideorthocarboxylic acid" of Graebe and Schultess. It melted at 267° – 268° and contained no water of crystallization, while the acid prepared by Graebe and Schultess contained $1\text{H}_2\text{O}$, melted at 99° , lost its water of crystallization at 105° and, after dehydrating, melted at 152° . Canter also prepared salts of orthophenylsulphonebenzoic acid, besides the chloride, amide and anilide and, finally, by treatment of the chloride with benzene and aluminum chloride, he obtained orthobenzoyldiphenylsulphone, which he showed to be identical with the substance obtained by Remsen and Saunders¹ from the mixed chlorides of orthosulphobenzoic acid, benzene and aluminum chloride:



This last reaction was accepted as proof of the structure of orthophenylsulphonebenzoic acid on the one hand and of orthobenzoyldiphenylsulphone on the other. It remained, then, to ascertain the cause of the difference between the "orthophenylsulphonebenzoic acid" of Canter and the "sulphobenzideorthocarboxylic acid" of Graebe and Schultess.

The two compounds are clearly different and as the plausibility of the structure assigned to each is so great, this investigation was undertaken with the view of studying the oxidation-product of phenylthiosalicylic acid more closely, in the hope that the cause of the discrepancy might thus be found.

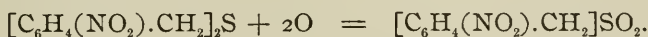
As a possible explanation it appeared that Graebe and Schultess might have isolated the sulfoxide instead of the sulphone.

¹ THIS JOURNAL, 17, 362.

But few cases are known in which nitric acid is able to oxidize an aromatic sulphide to a sulphone, notably the following :

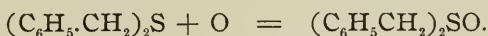
Stenhouse¹ showed that phenyl sulphide is changed into diphenylsulphone when heated, during 1-2 hours, with strong nitric acid.

Jahoda² succeeded in preparing orthonitrobenzylsulphone by heating orthonitrobenzyl sulphide, with fuming nitric acid, in a sealed tube, at 150° :



Ordinary concentrated nitric acid, however, gave rise to the sulphoxide and potassium permanganate, in excess, gave the sulphone.

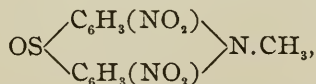
Potassium permanganate accomplishes the transformation to the sulphone in many cases when nitric acid produces only the sulphoxide or nitrosulphoxide ; for example, Märcker³ showed that benzyl sulphide is oxidized to benzyl sulphoxide, by treatment with cold nitric acid (sp. gr. 1.3) :



If heat is applied during the reaction, benzoic and sulphuric acids result.

On the other hand, potassium permanganate converts benzyl sulphide into benzyl sulphone.⁴

Methyldiphenylamine sulphide, $\text{S} \begin{matrix} \diagup \text{C}_6\text{H}_4 \\ \diagdown \text{C}_6\text{H}_4 \end{matrix} \text{N}.\text{CH}_3$, is transformed into dinitromethyldiphenylaminesulphoxide,⁵



by the action of fuming nitric acid, whereas, by means of potassium permanganate, the sulphone,

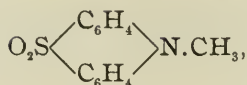
¹ Ann. Chem. (Liebig), 140, 290.

² Monats. Chem., 10, 81.

³ Ann. Chem. (Liebig), 136, 89.

⁴ Otto and Lüders : Ber. d. chem. Ges., 13, 1284.

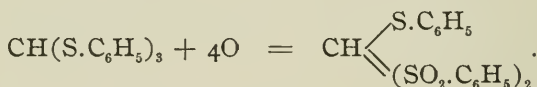
⁵ Bernthsen : Ann. Chem. (Liebig), 230, 73.



is obtained.

The formation of nitrosulphoxides is also observed when diphenylamine sulphide, $\text{S} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{C}_6\text{H}_4 \diagup \end{array} \text{NH}$, and acetyldiphenylamine sulphide, $\text{S} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{C}_6\text{H}_4 \diagup \end{array} \text{N}(\text{C}_2\text{H}_5\text{O})$, are treated with fuming nitric acid.

When phenyl thiorthoformate¹ is treated with potassium permanganate, in acid solution, a disulphone results :

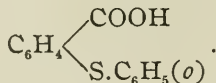


If alkaline permanganate is used the trisulphone, $\text{CH}(\text{SO}_2 \cdot \text{C}_6\text{H}_5)_3$, is obtained. When treated with nitric acid the sulphide yields an unidentified substance containing nitrogen.

In 1895, Bourgeois² stated that he was studying the action of nitric acid, of various concentrations, upon organic sulphides, but as yet no paper by him upon this subject has appeared.

II. OXIDATION OF PHENYLTHIOSALICYLIC ACID WITH NITRIC ACID.

1. Preparation of Phenylthiosalicylic Acid,



Thiophenol is best prepared by the method of Winter³ which is a modification of that of Otto.⁴

¹ Ber. d. chem. Ges., **23**, 1416; **25**, 348.

² *Ibid.*, **28**, 2322.

³ THIS JOURNAL, **31**, 572.

⁴ Ber. d. chem. Ges., **10**, 3055.

The thiophenol used in this investigation was colorless and boiled at 168° (uncor.).¹

A mixture of 34 grams of thiophenol, 60 grams of sodium hydroxide and 300 cc. of water is warmed at 50° . To this the diazotized anthranilic acid is added, from a dropping-funnel, in a thin stream. For the diazotization, 40 grams of anthranilic acid, 22 grams of sodium nitrite, 64 cc. of concentrated hydrochloric acid and 200 cc. of water are used, the temperature being kept at 2° – 5° .

When the sodium thiophenolate is treated with the ortho-diazoniumbenzoic acid chloride the alkaline solution becomes red and nitrogen is evolved. After this has ceased, the flask is warmed on a water-bath for an hour, or until all the nitrogen is given off. After cooling, the solution is acidified and phenylthiosalicylic acid is precipitated as a red, pasty mass, which becomes solid. It is dissolved in sodium carbonate solution and warmed slightly. The cooled solution is filtered from the phenyl disulphide, which is always formed by the oxidation of thiophenol. These residues of phenyl disulphide can be used in preparing thiophenol, by simply heating with zinc dust and acidifying. The filtrate is again acidified carefully and the phenylthiosalicylic acid appears as a voluminous, reddish mass. This is pulverized, after it has hardened, then washed well with water and dried on a porous plate.

From 40 grams of anthranilic acid 65–70 grams of the crude product are obtained; the theoretical yield is 74 grams.

In order to purify the substance it is best to proceed as follows:

Dissolve in hot alcohol until the solution is quite concentra-

¹ The experience of the writer with thiophenol leads him to give a brief description of its physiological effects. As is well known, in concentrated form, it produces severe burns, but even after a momentary contact with the skin very unpleasant and dangerous effects may follow. After ten days or more, an eruption appears at the point of contact, accompanied by severe itching. The affected part becomes red and much swollen, suppurating pustules appear and, in severe cases, symptoms of blood-poisoning manifest themselves. The treatment is, in general, that for a severe burn: exclusion of air and moisture and use of an antiseptic ointment. The vapors of thiophenol, when present in considerable amount, produce giddiness and headache and have a remarkable effect upon the eyes. The lids droop and it is impossible to raise them. After a few minutes in the fresh air, this effect passes off, but the eyes remain very sensitive to light.

ted. Allow to cool partially, until the fine crystals which separate convert the liquid almost into a solid. Filter the crystals, using a Witt plate or Büchner funnel, separating the deeply-colored mother-liquor as completely as possible. Wash several times with cold alcohol. It will be found that but a few crystallizations are necessary to bring the acid to a state of comparative purity, if the mother-liquor is thoroughly removed and the crystals well washed each time. For the last crystallizations it is best to use alcohol of about 60 per cent. The residues contained in the mother-liquors may, to a certain extent, be recovered, but a quantity of black, tarry material is always present. The yield of purified product is 20 grams from the above quantities.

Phenylthiosalicylic acid is colorless, melts at 166° and, when heated gently, sublimes easily without decomposition, being deposited in leaflets. If heated at about 300° , it distils and decomposes into thioxanthone, which collects in the receiver in beautiful yellow needles melting at 207° . The same transformation is effected by warming with concentrated sulphuric acid, in which it dissolves with a very deep green fluorescence.

Phenylthiosalicylic acid crystallizes from alcohol in leaflets. It is almost insoluble in cold water, slightly so in hot water; easily soluble in benzene, methyl, ethyl and propyl alcohols, ether and fairly so in glacial acetic acid.

Graebe and Schultess describe the potassium, ammonium and silver salts and the ethyl ester. The barium salt is quite soluble, but apparently is incapable of being crystallized.

Analysis :

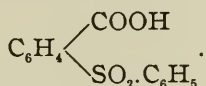
0.1474 gram substance gave 0.3643 gram CO_2 and 0.0587 gram H_2O .

0.1015 gram substance gave 0.1049 gram BaSO_4 .

	Calculated for $\text{C}_6\text{H}_4 \begin{array}{l} \nearrow \text{COOH} \\ \searrow \text{S.C}_6\text{H}_5 \end{array}$	Found.
C	67.78	67.40
H	4.39	4.45
S	13.93	14.19

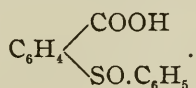
2. *Oxidation of Phenylthiosalicylic Acid by Means of Dilute Nitric Acid.*

Graebe and Schultess state that when phenylthiosalicylic acid was heated with dilute nitric acid (1 part concentrated nitric acid to 2 parts water), they obtained an acid which crystallized from alcohol in white needles, containing 1 molecule of water of crystallization and melting at 99° . At 105° this substance lost its water and, after being dehydrated, it melted at 152° . From the method of its formation and the results of analyses they called it sulphobenzideorthocarboxylic acid and considered its formula to be :



They did not make any salts or other derivatives.

We repeated the work of Graebe and Schultess, and obtained, as a product of treating phenylthiosalicylic acid with dilute nitric acid, an acid which we identified as diphenylsulphoxide-orthocarboxylic acid, having the formula :



Ten grams of phenylthiosalicylic acid were treated, in a large test-tube, with 40 cc. of dilute nitric acid (1 vol. concentrated acid to 2 vols. water) and the mixture boiled. The material becomes darker and oily, brown fumes are given off and finally the oil, which at first goes into solution, separates and sinks to the bottom. The heating is stopped, water is added and the material allowed to solidify. It is then pulverized and washed. Treatment, upon the filter, with small quantities of ether, removes some reddish impurities, leaving a yellow mass which is then crystallized from methyl alcohol. It can also be crystallized from ordinary alcohol, in which it is very soluble, being deposited in large rhombohedrons which tend to form parallel growths. From methyl alcohol the forms are more elongated and prismatic. As first obtained the crystals are yellow and melt at 161° – 162° . By repeated crystallization,

however, they become colorless and transparent, melting at 163° . By crystallization from dilute ethyl alcohol long, white needles are deposited. They are arranged in bunches and greatly resemble the product described by Graebe and Schultess; in fact, as both may be present in the solution, it is very difficult, in many cases, to say whether the product is homogeneous; but, if the rhombohedra are recrystallized from very dilute alcohol the needles are obtained; these consist of diphenylsulphoxideorthocarboxylic acid containing 1 molecule of water of crystallization. When crystallized from water the same result is observed, but the hydrated form tends to pass back to the anhydrous, rhombohedral modification while in contact with water.

The hydrated form has not a definite melting-point. It begins to soften at about 80° – 85° , losing water of crystallization at 100° – 105° and melting completely at 164° . If heated suddenly, however, to a temperature of 80° – 90° , it melts and foams. Recrystallization of the hydrated, needle form of the acid from pure methyl or ethyl alcohol gives the anhydrous rhombohedra. Diphenylsulphoxideorthocarboxylic acid is quite easily soluble in ordinary alcohol, somewhat less so in methyl alcohol. It is very soluble in propyl alcohol, readily so in chloroform and with difficulty in ether. Hot water dissolves it very sparingly and in cold water it is practically insoluble. It is not changed by heating with concentrated, or fuming nitric acid. Heated with concentrated sulphuric acid it dissolves, forming a red liquid, with a very deep green fluorescence. With the hope of obtaining a compound analogous to thioxanthone, this solution was heated for several hours at 110° and, after cooling, poured into water. The dark-colored material which separated did not, however, seem capable of crystallization.

Analysis of the anhydrous acid :

I. 0.1812 gram substance gave 0.0647 gram H_2O and 0.4217 gram CO_2 .

II. 0.2035 gram substance gave 0.0711 gram H_2O and 0.4693 gram CO_2 .

III. 0.1620 gram substance gave 0.1581 gram $BaSO_4$.

IV. 0.1873 gram substance gave 0.18195 gram $BaSO_4$.

	Calculated for $\text{C}_6\text{H}_4 \begin{cases} \text{COOH} \\ \text{SO} \cdot \text{C}_6\text{H}_5 \end{cases}$	I.	Found.	II.
C	63.38	63.46		62.89
H	4.10	3.99		3.91
S	13.02	13.40		13.36

As it is impossible to obtain the hydrated acid free from the anhydrous, an accurate determination of the water of crystallization could not be made. The best specimen obtained gave the following :

0.2024 gram air-dried acid lost in weight, at 105° , 0.0133 gram.

	Calculated for $\text{C}_6\text{H}_4 \begin{cases} \text{COOH} \\ \text{SO} \cdot \text{C}_6\text{H}_5 \end{cases} \cdot \text{H}_2\text{O}$	Found.
H_2O	6.82	6.08

Salts of Diphenylsulphoxideorthocarboxylic Acid.

Barium Salt.—This was prepared in the usual manner, by digesting the acid with water and excess of barium carbonate, filtering and evaporating to crystallization. White needles or prisms are deposited, which are often arranged in bunches.

Analysis :

0.1538 gram air-dried salt lost, at 110° , 0.0229 gram H_2O .

0.2426 gram air-dried salt lost, at 110° , 0.0447 gram H_2O .

0.14645 gram salt, dried at 110° , gave 0.0533 gram BaSO_4 .

0.1690 gram salt, dried at 110° , gave 0.0623 gram BaSO_4 .

0.1758 gram salt, dried at 110° , gave 0.0646 gram BaSO_4 .

	Calculated for $\left(\text{C}_6\text{H}_4 \begin{cases} \text{COO} \\ \text{SO} \cdot \text{C}_6\text{H}_5 \end{cases} \right)_2 \text{Ba} \cdot 8\text{H}_2\text{O}$	I.	Found.	II.
H_2O	18.65	18.85		18.47

	Calculated for $\left(\text{C}_6\text{H}_4 \begin{cases} \text{COO} \\ \text{SO} \cdot \text{C}_6\text{H}_5 \end{cases} \right)_2 \text{Ba}$	I.	Found.	III.
Ba	21.89	21.42	21.69	21.62

Strontium Salt.—This was prepared like the barium salt which it resembles closely and with which it is, apparently, isomorphous. The crystals are efflorescent, so an accurate determination of the water could not be made.

Analysis :

0.2235 gram crystallized salt lost, at 110°, 0.0435 gram H₂O.

0.2516 gram crystallized salt lost, at 110°, 0.0491 gram H₂O.

0.2025 gram salt, dried at 110°, gave 0.0636 gram SrSO₄.

0.1869 gram salt, dried at 110°, gave 0.0583 gram SrSO₄.

	Calculated for $\left(\text{C}_6\text{H}_4 \begin{array}{l} \text{COO} \\ \text{SO.C}_6\text{H}_5 \end{array}\right)_2\text{Sr.8H}_2\text{O}.$	I.	Found.	II.
H ₂ O	19.95	19.46	19.51	
	Calculated for $\left(\text{C}_6\text{H}_4 \begin{array}{l} \text{COO} \\ \text{SO.C}_6\text{H}_5 \end{array}\right)_2\text{Sr}.$	I.	Found.	II.
Sr	15.17	14.93	14.90	

Calcium Salt.—This was prepared like the strontium and barium salts. It is, apparently, isomorphous with them and crystallizes in groups of needles or prisms. Analysis :

0.2774 gram crystallized salt lost, at 110°, 0.0508 gram H₂O.

0.1966 gram salt, dried at 110°, gave 0.0503 gram CaSO₄.

	Calculated for $\left(\text{C}_6\text{H}_4 \begin{array}{c} \text{COO} \\ \text{SO.C}_6\text{H}_5 \end{array}\right)_2\text{Ca.8H}_2\text{O}.$	Found.
H ₂ O	21.36	20.53
	Calculated for $\left(\text{C}_6\text{H}_4 \begin{array}{c} \text{COO} \\ \text{SO.C}_6\text{H}_5 \end{array}\right)_2\text{Ca}.$	Found.
Ca	7.55	7.37

3. Oxidation of Phenylthiosalicylic Acid with Fuming Nitric Acid.

Graebe and Schultess, by the action of dilute nitric acid on phenylthiosalicylic acid, obtained a product to which they as-

signed the formula $\text{C}_6\text{H}_4 \begin{array}{l} \text{COOH} \\ \text{SO}_2.\text{C}_6\text{H}_5 \end{array}$. Upon repeating their

experiment and following, as closely as possible, the meager directions given, it was found that, in most cases, the compound described above as the sulphoxide was obtained in large quantity, but frequently very little of the desired substance could be isolated. By the use of concentrated or fuming nitric acid,

the product is almost wholly the one described by Graebe and Schultess.

To 10 grams of phenylthiosalicylic acid about 10 cc. of fuming nitric acid are added slowly. Violent action takes place immediately and a clear, dark-red solution is obtained. If ordinary concentrated nitric acid is used it is necessary to heat in a water-bath for a few minutes, to effect complete solution. The product is poured into water and the oil which separates allowed to solidify; this may be hastened by rubbing with a pestle, under cold water. The yellowish mass is then pulverized, washed well with water and treated, on the filter, with small quantities of ether to remove the reddish impurities. The product is almost perfectly white; it is dissolved in warm alcohol, in which it is very soluble, the solution is red. A few cc. of water are added and the liquid is allowed to crystallize.

Fine, white needles, arranged in bunches, are deposited and, if not too dilute, the liquid will become almost solid. These crystals melt at 99° and, when dehydrated at 105° , melt again at 152° . The yield is 7.5 grams from 10 grams of phenylthiosalicylic acid.

When recrystallized from slightly diluted alcohol the compound is unchanged and appears to be perfectly uniform, but after the third or fourth crystallization a decided difference is observed; in addition to the needles, a white, pulverulent substance is deposited which does not dissolve so readily in tepid alcohol and can thus be separated from the other compound. Continuation of the crystallization gives the same result and the needles no longer melt at 99° , but soften much lower (about 85°) and melt completely only at 156° – 163° . Recrystallization of the pulverulent material from alcohol gives leaflets, melting at 216° .

When the compound melting at 99° was digested with water and barium carbonate, for the purpose of preparing the barium salt, two products resulted; one was found to be barium diphenylsulphoxideorthocarboxylate and the other the barium salt of the acid melting at 216° . The same was observed in the case of the strontium and calcium salts.

It appears, then, that the product described by Graebe and Schultess is composed of two acids, diphenylsulphoxideortho-carboxylic acid and the acid melting at 216° .

The latter is formed only to a small extent under these conditions, but by boiling the solution of phenylthiosalicylic acid in fuming nitric acid for some time, the yield was much increased. As a result of several experiments the following method was adopted.

Ten grams of phenylthiosalicylic acid are placed in a small flask and 20 cc. of fuming nitric acid are added gradually. After the first violent action has subsided and the phenylthiosalicylic acid has dissolved, the flask is attached to a reflux condenser and heated on the water-bath for 3 hours. When cool, the solution is poured into water. A yellow oil separates, which partly solidifies after several hours. The sticky, semi-solid mass is heated in an air-bath, at 110° , for an hour and is then dissolved in boiling benzene, in which it is difficultly soluble. From this solution, small, colorless crystals separate, together with a gummy product which adheres to them. The mother-liquor is poured off and the residue washed with small portions of boiling benzene, which removes the gum. The crystals, as thus obtained, melt at 216° (uncor.), the corrected melting-point being 222° . A qualitative test of the acid melting at 216° indicated the presence of nitrogen and a determination, by the absolute method of Dumas, gave the following results:

6.2437 gram substance gave 10.95 cc. = 0.01258 gram N.

	Calculated for	
	$(\text{NO}_2) \cdot \text{C}_6\text{H}_3 \begin{cases} \text{COOH} \\ \text{SO} \cdot \text{C}_6\text{H}_5 \end{cases}$	
N	4.82	Found. 5.15

The *barium salt*, prepared in the usual way, consists of fine prisms or of wart-like masses, very difficultly soluble in water.

Analysis:

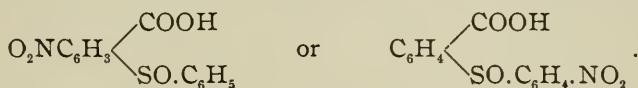
0.1268 gram crystallized salt lost 0.0016 H_2O at 130° .

	Calculated for	
	$\left(\text{C}_6\text{H}_4 \begin{cases} \text{COO} \\ \text{SO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 \end{cases} \right)_2 \text{Ba} \cdot 6\text{H}_2\text{O}$	
H_2O	1.31	Found. 1.29

0.1252 gram salt, dried at 130°, gave 0.0400 BaSO₄.

	Calculated for	
	$\left(\text{C}_6\text{H}_4 \begin{array}{l} \text{COO} \\ \text{SO.C}_6\text{H}_4.\text{NO}_2 \end{array} \right) \text{Ba.}$	
Ba	19.16	Found. 18.80

From this it is evident that the acid melting at 216° (uncor.) is a mononitro derivative of diphenylsulphoxideorthocarboxylic acid. No attempt was made to determine the position of the nitro group. The formula of the acid may be



When the benzene mother-liquor, from which the nitro compound had crystallized, was evaporated to dryness, a gummy substance remained. This was dissolved in boiling ethyl acetate, from which a relatively large quantity of small, white leaflets crystallized on cooling. This substance melted at 163° (uncor.) and was diphenylsulphoxideorthocarboxylic acid.

It was found that a mixture of this acid with a small proportion of the mononitro derivative crystallizes from alcohol in white needles, melting at 99°, losing water at 105° and melting again at 152°. It appears, from this, that the acid described by Graebe and Schultess, melting at 99°, is not a definite compound, but a mixture of diphenylsulphoxideorthocarboxylic acid and a mononitrodiphenylsulphoxideorthocarboxylic acid.

The yield of nitrodiphenylsulphoxideorthocarboxylic acid is small, even when the method of preparation just described is used and an attempt was, therefore, made to increase it.

Phenylthiosalicylic acid was treated with fuming nitric acid as before. The solution was cooled and 2 volumes of concentrated sulphuric acid added. The flask was then attached to a reflux condenser and heated for 3 hours on the water-bath. After cooling, the reaction mixture was poured into water. A yellowish-white, semi-solid mass separated. The acid solution was separated and the residue boiled with a little water, to remove the nitric and sulphuric acids. After cooling, the gummy mass was dried in an air-bath, at 130°,

for several hours. It solidified on cooling and was pulverized and boiled with benzene. Most of it dissolved, the residue was filtered off and dissolved in alcohol, from which it separated, on the addition of water, in very small, white crystals, melting at about 208° . The product was evidently not homogeneous and it was not found possible to purify it. The *barium salt* was made and analysis indicated its derivation from a mixture of dinitro- and trinitrodiphenylsulphoxideorthocarboxylic acids, with, perhaps, some of the mononitro compound. Analyses :

0.2436 gram air-dried salt lost 0.0271 gram H_2O at 180° .

H_2O

11.12

I. 0.1793 gram anhydrous salt gave 0.0489 gram $BaSO_4$.

II. 0.1271 gram anhydrous salt gave 0.0349 gram $BaSO_4$.

	Calculated for		Found.	
	$(C_{13}H_7O_3S(NO_2)_2)_2Ba.$	$(C_{13}H_6O_3S(NO_2)_3)_2Ba.$	I.	II.
Ba	17.02	15.28	16.05	16.06

The acid melting at about 208° was analyzed by the absolute method.

0.1845 gram substance gave 15.00 cc. $N = 0.0173$ gram N .

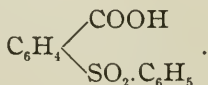
	Calculated for		Found.
	$C_{13}H_6O_3S(NO_2)_2.$	$C_{13}H_7O_3(NO_2)_3.$	
N	8.36	12.53	9.39

Owing to lack of time this product was not studied further.

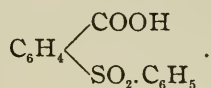
III. DIPHENYLSULPHONEORTHOCARBOXYLIC ACID.

1. Oxidation of Phenylthiosalicylic Acid by Means of Potassium Permanganate.

By the use of potassium permanganate it was hoped that the sulphone obtained by Canter would be formed. The product is, however, not identical with that sulphone, although its general reactions and analyses seem to show that it should be represented by the formula



These facts will be discussed later.

Diphenylsulphoneorthocarboxylic Acid,

For the preparation of this acid either phenylthiosalicylic acid or diphenylsulphoxideorthocarboxylic acid may be used. The products were carefully examined and proved to be identical.

Ten grams of phenylthiosalicylic acid were placed in a 3-liter round flask, containing about 2 liters of water. The flask was heated on a water-bath, while steam was passed in and finely ground potassium permanganate added from time to time, in small portions, until slightly more than the calculated amount had been used. The oxidation proceeded rapidly and was usually complete in about an hour and a half. The excess of permanganate is reduced by means of a few drops of alcohol and, after filtration, the solution is evaporated to 100–200 cc. After cooling, diphenylsulphoneorthocarboxylic acid is precipitated as an oil, by addition of hydrochloric acid, solidification being induced by rubbing with a pestle, under cold water. The white mass is then pulverized and washed well with water. It is best crystallized from benzene, from which it is deposited in white needles, melting at 143°. Other solvents are unsatisfactory for its crystallization. It is extremely soluble in methyl, ethyl and propyl alcohols, ether, glacial acetic acid and acetone; almost insoluble in water and ligroin. With care it can be crystallized from alcohol or acetic acid, by the addition of water, but in most cases it appears as an oil. When deposited as crystals from these mixtures, it forms clusters of needles, which, if pressed quickly between filter-paper and the melting-point taken immediately, do not melt at 143°, but often much lower, usually near 100°. If allowed to stand in contact with the air for a short time, the higher melting-point is obtained. This seems to indicate that water of crystallization is present, but is lost upon exposure to the air. When heated with water alone, some of the acid dissolves and, upon cooling, these same crystals are obtained, together with the syrup. If a great deal of

water is used and the solution allowed to evaporate slowly, beautiful clear prisms are frequently deposited, which seem to be of the triclinic or rhombohedral-hexagonal system. They contain $1.5 \text{ H}_2\text{O}$, are efflorescent and melt at $51^\circ.5$.

The reactions of diphenylsulphoneorthocarboxylic acid show it to be a stable substance. Apparently no decomposition takes place at 190° ; above this some volatile products are formed, but high heat is necessary to cause any marked change in color. It is unchanged by dilute or concentrated nitric acid.

When fused for several hours, in a silver crucible, with potassium hydroxide, at 180° or at 210° , it is decomposed, an odor similar to that of diphenyl being observed during the fusion. After cooling, the residue dissolves in water and, on acidifying, the odors of phenol, thiophenol and sulphur dioxide were noticed and the solution became milky. Evaporation of the liquid to a small volume yielded fine, white crystals which were recrystallized from alcohol; white needles or prisms of salicylic acid were obtained, which melted at 155° – 156° and gave the color reaction with ferric chloride. These products are what we should expect from a substance having the formula given above.

No change was observed in the properties of diphenylsulphoneorthocarboxylic acid when it is boiled, with aqueous potassium hydroxide, for 6 hours, or for 2 hours with pyridine, in which it is very soluble.

Heated with concentrated sulphuric acid it dissolves, giving a beautiful fluorescence and is transformed into benzophenone-sulphone.

In alcoholic solution the acid does not rotate the plane of polarization.

The corresponding compound, prepared by Canter and designated orthophenylsulphonebenzoic acid, is readily soluble in alcohol and crystallizes in small, clear plates. The melting-point given is 267° – 268° (uncor.). Differences are also observed when the salts of the two acids are compared.

Analysis of the rhombohedral crystals, obtained from aqueous

solution and of the anhydrous acid, gave the following results :

0.2002 gram acid, melting at $51^{\circ}.5$, lost, at 110° , 0.0183 gram H_2O .

0.1828 gram acid, melting at $51^{\circ}.5$, lost, at 110° , 0.0179 gram H_2O .

	Calculated for $C_6H_4 \begin{matrix} \swarrow COOH \\ \searrow SO_2.C_6H_5 \end{matrix} .1\frac{1}{2}H_2O.$	I.	Found. II.
H_2O	9.35	9.14	9.79

0.1986 gram anhydrous acid gave 0.4329 gram CO_2 and 0.0656 gram H_2O .

0.2177 gram of anhydrous acid gave 0.4699 gram CO_2 and 0.0721 gram H_2O .

0.2144 gram of anhydrous acid gave 0.1878 gram $BaSO_4$.

0.1927 gram of anhydrous acid gave 0.1703 gram $BaSO_4$.

	Calculated for $C_6H_4 \begin{matrix} \swarrow COOH \\ \searrow SO_2.C_6H_5 \end{matrix}$	I.	Found. II.
C	59.51	59.44	58.86
H	3.85	3.70	3.77
S	12.23	12.09	12.14

Salts of Diphenylsulphoneorthocarboxylic Acid.

Calcium Salt.—When this is deposited, slowly, from solution it forms beautiful pearly plates, arranged in clusters, containing 9 molecules of water. Care must be used in crystallizing the salt, otherwise a mixture results, with a variable amount of water of crystallization.

The salt loses nearly all its water of crystallization at 115° , but does not give up the last portion—apparently half a molecule—below 175° . This at first caused an error in the analysis of the salt, the percentage of calcium being found to be low. The dehydration of the salt was studied more carefully, with the result mentioned.

0.2156 gram of crystallized salt lost in weight, at 115° , 0.0469 gram and, at 175° , 0.0479 gram.

0.1941 gram of crystallized salt lost in weight, at 115° , 0.0420 gram and, at 175° , 0.0429 gram.

0.1677 gram dry salt gave 0.0407 gram BaSO_4 .

0.1512 gram dry salt gave 0.0363 gram BaSO_4 .

	Calculated for		Found.	
	$\left(\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{COO} \\ \diagdown \text{SO}_2 \cdot \text{C}_6\text{H}_5 \end{array} \right)_2 \text{Ca} \cdot 9\text{H}_2\text{O}.$	I.		II.
$8\frac{1}{2} \text{H}_2\text{O}$	21.77	21.75		21.63
$9 \text{H}_2\text{O}$	22.37	22.21		22.10

	Calculated for		Found.	
	$\left(\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{COO} \\ \diagdown \text{SO}_2 \cdot \text{C}_6\text{H}_5 \end{array} \right)_2 \text{Ca}.$	I.		II.
Ca	7.11	7.14		7.06

Barium Salt.—This crystallizes in groups of needles, which are possibly not uniform, consisting apparently of hydrous and anhydrous salt. Determinations of the water of crystallization are, therefore, unreliable. All the water is not completely expelled below 175° . This is probably similar to the case of the calcium salt.

0.1755 gram crystallized salt lost in weight, at 120° , 0.0040 gram.

0.1755 gram crystallized salt lost in weight, at 175° , 0.0058 gram.

0.2295 gram crystallized salt lost in weight, at 175° , 0.0076 gram.

0.1998 gram crystallized salt lost in weight, at 175° , 0.0068 gram.

0.2219 gram dried salt gave 0.0781 gram BaSO_4 .

0.1930 gram dried salt gave 0.0681 gram BaSO_4 .

	Calculated for		Found.	
	$\left(\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{COO} \\ \diagdown \text{SO}_2 \cdot \text{C}_6\text{H}_5 \end{array} \right)_2 \text{Ba} \cdot 1\frac{1}{2}\text{H}_2\text{O}.$	I.	II.	III.
H_2O	2.66	2.28	.	.
$1\frac{1}{2}\text{H}_2\text{O}$	3.93	3.30	3.31	3.40
	Calculated for		Found.	
	$\left(\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{COO} \\ \diagdown \text{SO}_2 \cdot \text{C}_6\text{H}_5 \end{array} \right)_2 \text{Ba}.$	I.		II.
Ba	20.83	20.71		20.77

Strontium Salt.—As in the case of the barium salt, a sufficiently uniform rate of deposition is very difficult to obtain, in consequence of which the quantity of water of crystal-

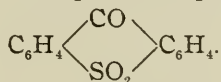
lization is possibly unreliable. The salt is not completely dehydrated below 185° and no accurate determinations of the amount of water retained at lower temperatures could be made.

0.2198 gram crystallized salt lost in weight, at 185° , 0.0398 gram.

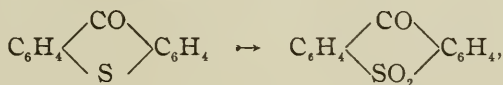
0.1800 gram dehydrated salt gave 0.0535 gram SrSO_4 .

	Calculated for $\left(\text{C}_6\text{H}_4 \begin{array}{l} \text{COO} \\ \text{SO}_2\text{C}_6\text{H}_5 \end{array} \right)_2 \text{Sr} \cdot 7\frac{1}{2} \text{H}_2\text{O}.$	Found.
$7\frac{1}{2} \text{H}_2\text{O}$	18.14	18.18
	Calculated for $\left(\text{C}_6\text{H}_4 \begin{array}{l} \text{COO} \\ \text{SO}_2\text{C}_6\text{H}_5 \end{array} \right)_2 \text{Sr}.$	Found.
Sr	14.35	14.20

2. *Benzophenonesulphone*,



This substance was first described by Beckmann,¹ who obtained it as a by-product in the treatment of benzophenone with fuming sulphuric acid. Graebe and Schultess² obtained it by the oxidation of thioxanthone by means of chromic acid,



and showed it to be identical with Beckmann's product. It occurred to us to try the action of concentrated sulphuric acid upon diphenylsulphoneorthocarboxylic acid, in order, if possible, to effect a dehydration similar to that accomplished in the case of phenylthiosalicylic acid. Several grams were heated at 125° , for 14 hours, with concentrated sulphuric acid. After cooling, the material was poured into cold water and the caseous precipitate was filtered, washed, dissolved in alcohol and allowed to crystallize. Very long, clear, slightly yellow prisms were deposited, which melted at $184^{\circ}.5$.

The color reactions given by Graebe and Schultess for the

¹ Ber. d. chem. Ges., 6, 1112; 8, 992.

² Ann. Chem. (Liebig), 263, 1.

identification of this compound were fully verified. Upon being heated with alcohol and strong potassium hydroxide a deep blue coloration is formed, which disappears when the solution is cooled and reappears when heated. By heating with aqueous alkali and zinc dust the same color is developed, but is destroyed by continued action. If the solution is filtered and allowed to stand, fine crystals appear.

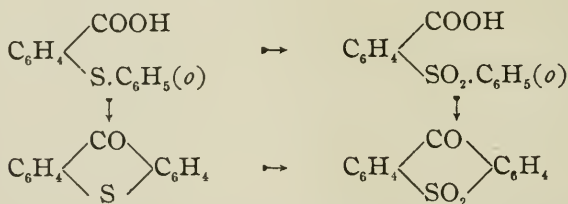
Benzophenonesulphone gives other color reactions. When heated with phenol and concentrated sulphuric acid, for a few minutes and then dissolved in alkali, a pink color is developed on warming which disappears when the solution is cooled. If heated with resorcinol and concentrated sulphuric acid and the product dissolved in dilute sodium hydroxide, the solution becomes red with a deep-green fluorescence.

Analysis :

0.1294 gram substance gave 0.3023 gram CO_2 and 0.0401 gram H_2O .

	Calculated for $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{SO}_2 \diagup \end{array} \text{C}_6\text{H}_4$	Found.
C	63.90	63.86
H	3.31	3.62

Benzophenonesulphone was also prepared by the method of Graebe and Schultess, from thioxanthone and was found to be identical with that prepared from diphenylsulphoneorthocarboxylic acid. Thus we have the following relation established between phenylthiosalicylic acid and diphenylsulphoneorthocarboxylic acid :



A further proof of the relation between phenylthiosalicylic acid and diphenylsulphoneorthocarboxylic acid is furnished by the following experiment :

(a) An intimate mixture of phenylthiosalicylic acid with 6 times its weight of powdered lime, was heated in a small retort. A yellow oil distilled over and feathery needles appeared in the distillate, this being due, probably, to the sublimation of some phenylthiosalicylic acid. The distillate was washed with sodium carbonate solution, to remove this unchanged phenylthiosalicylic acid, the yellow oil extracted with ether, dried and distilled. After the ether had passed off the temperature rose rapidly to 286° . The portion which came over between 286° and 292° was collected. Pure phenylsulphide boils at $292^{\circ}.5$ (Stenhouse). The distillate was a yellow oil and had an odor suggestive of volatile sulphides. It was dissolved in concentrated sulphuric acid, warmed gently and chromic anhydride added, in small portions, until the solution showed a reddish color. The mixture was then poured into cold water, the yellow precipitate filtered, washed, dried and dissolved in benzene, from which it crystallized in rhombic plates. Recrystallized from alcohol, it was obtained pure in colorless, rhombic plates, which melted at 124° (uncor.) ; 126° (cor.).

(b) In the same manner, diphenylsulphoneorthocarboxylic acid was heated with lime. A yellow oil distilled over, which solidified, on cooling, to a yellow crystalline mass. It was dissolved in benzene, from which it crystallized in rhombic plates. These were recrystallized from alcohol and formed colorless, rhombic plates, melting at 124° (uncor.) ; 126° (cor.).

A mixture of the two specimens, thus prepared, showed no change in the melting-point.

The melting-point of pure diphenylsulphone is $123^{\circ}.75$ (uncor.).¹

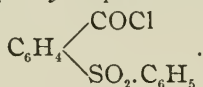
The conclusions from these experiments may be expressed thus :

¹ The question of the melting-point of diphenylsulphone has been very carefully investigated by Mr. Bradshaw, in this laboratory, during the present year. He found that the melting-point is $123^{\circ}.75$ (uncor.) no matter by what method the sulphone is obtained, if its purification is complete. The melting-point of diphenylsulphone is variously recorded, the values ranging from 124° – 128° (uncor.).



Considering the results in connection with the formation of benzophenonesulphone, as described above, there can be no doubt that the structure of diphenylsulphoneorthocarboxylic acid is really as represented.

3. *Chloride of Diphenylsulphoneorthocarboxylic Acid,*



This compound was prepared by treating the free acid with phosphorus pentachloride, in slight excess of the calculated amount. No change was observed at the ordinary temperature, but by heating upon the water-bath the reaction proceeded rapidly, the whole becoming liquid and bright red. The mass was then heated in a sulphuric-acid bath, to 125°, for several hours, to expel phosphorus oxychloride.

After cooling, it is treated with ice-water, pulverized, washed with ice-water and dried between sheets of bibulous paper. The color fades rapidly as the compound becomes dry and when perfectly free from water it is colorless. The chloride crystallizes well from ether in long, clear, colorless prisms or needles, which melt at 79° (uncor.) ; 80° (cor.). It is easily soluble in ether and benzene, with difficulty in ligroin. It is very stable and is not acted on by cold dilute alkali. It dissolves sparingly in boiling dilute alkali and diphenylsulphoneorthocarboxylic acid is precipitated on acidifying. A specimen of the chloride was exposed to the air for 3 weeks, but the melting-point was not changed.

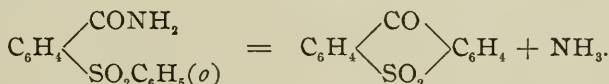
The chlorine was determined by boiling with aqueous potassium hydroxide, for 1 hour, acidifying with nitric acid and treating with silver nitrate.

0.1430 gram chloride gave 0.0711 gram AgCl.

	Calculated for $\begin{array}{c} \text{C}_6\text{H}_4 \begin{array}{l} \nearrow \text{COCl} \\ \searrow \text{SO}_2\text{C}_6\text{H}_5 \end{array} \end{array}$	Found.
Cl	12.63	12.29

4. Diphenylsulphoneorthocarboxylamide.

When diphenylsulphoneorthocarboxylic chloride is allowed to stand with concentrated ammonia, at the ordinary temperature, for 24 hours, the amide is formed, an appreciable amount of heat being evolved during the first few minutes. The solid product thus obtained is filtered, washed and dissolved in boiling water, filtering, if necessary, from any unchanged chloride. On cooling, the amide crystallizes in slender, pure-white needles, which form a semi-solid mass if the solution is not too dilute. These melt at 171° – 171.5° (uncor.) ; 175° – 175.5° (cor.). As is the case with all the derivatives of diphenylsulphoneorthocarboxylic acid, the amide is a very stable compound. It was found to be impossible to make a satisfactory determination of nitrogen by the Kjeldahl method, or by the Gunning modification, using sulphuric acid and potassium sulphate. When the latter was used benzophenonesulphone sublimed into the upper portion of the digestion-flask and was deposited in very fine crystals. This reaction may be expressed thus :



The determinations were, therefore, too low, by about 1.0–0.5 per cent. Dumas' absolute method gave a better result :

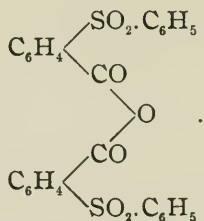
0.4215 gram amide gave 17.4 cc. N under standard conditions = 0.02176 gram N.

	Calculated for $\begin{array}{c} \text{C}_6\text{H}_4 \begin{array}{l} \nearrow \text{CONH}_2 \\ \searrow \text{SO}_2\text{C}_6\text{H}_5 \end{array} \end{array}$	Found.
N	5.37	5.16

5. Diphenylsulphoneorthocarboxylic Anhydride.

A mixture of 1 gram of diphenylsulphoneorthocarboxylic chloride with 1.2 grams of the acid was placed in a dry test-

tube and heated, in a sulphuric-acid bath, at 135° – 150° , for several hours. The mass became liquid and hydrochloric acid was evolved freely. After about 3 hours the tube was allowed to cool. The contents solidified to a dark-brown, crystalline mass, which was dissolved in boiling benzene, boiled with animal charcoal and filtered. On cooling, small, irregularly shaped, colorless crystals separated, which melted at 143° . The method of formation and the analyses of the substance show it to be the anhydride of diphenylsulphoneorthocarboxylic acid,



This anhydride is exceedingly stable towards alkali. Boiled for an hour with concentrated sodium hydroxide, there was no perceptible change. It dissolves in concentrated sulphuric acid and when this solution is heated at 130° , for 10 hours, the anhydride is converted into benzophenonesulphone. The product thus obtained was identical with that prepared by the similar treatment of diphenylsulphoneorthocarboxylic acid and also with that obtained by oxidizing thioxanthone. The anhydride is soluble in boiling alcohol, from which it crystallizes in small, hard, colorless crystals melting at 145° ; the crystals from the benzene solution melt at 143° . When equal portions of the anhydride, crystallized from benzene and from alcohol, respectively, are mixed the melting-point of the mixture is 144° . The corrected melting-point of the anhydride, from benzene, is 146° ; from alcohol, 148° .

Analyses:

I. 0.2483 gram substance gave 0.5580 gram CO_2 , and 0.0678 gram H_2O .

II. 0.2408 gram substance gave 0.5483 gram CO_2 , and 0.0760 gram H_2O .

III. 0.3035 gram substance gave 0.6901 gram CO_2 and 0.0909 gram H_2O .

	Calculated for $\left(\text{C}_6\text{H}_4 \begin{array}{l} \text{CO} \\ \text{SO}_2 \cdot \text{C}_6\text{H}_5 \end{array}\right)_2\text{O}$.	Found.		
		I.	II.	III.
C	61.64	61.28	62.09	62.00
H	3.58	3.03	3.50	3.35

see errata p. 647 6. Ethyl Diphenylsulphoneorthocarboxylate.

Two grams of the chloride were boiled, for a few minutes, with about 50 cc. of absolute ethyl alcohol. The chloride dissolved. Water was added, until precipitation was almost effected and the solution allowed to cool. Bunches of colorless, feathery, radial needles separated out after standing a short time. These melted at $77^\circ\text{--}78^\circ$ (uncor.); $78^\circ\text{--}79^\circ$ (cor.).

The ester is saponified, with some difficulty, by boiling with a 10 per cent solution of sodium hydroxide. Analysis:

0.2317 gram ester gave 0.5234 gram CO_2 and 0.1029 gram H_2O .

	Calculated for $\text{C}_6\text{H}_4 \begin{array}{l} \text{COOC}_2\text{H}_5 \\ \text{SO}_2 \cdot \text{C}_6\text{H}_5 \end{array}$	Found.
C	62.06	61.58
H	4.83	4.93

7. Methyl Diphenylsulphoneorthocarboxylate.

The chloride was boiled with methyl alcohol and water added to the solution, which was then allowed to cool. A slightly yellowish oil separated, which solidified on standing. Long, prismatic, tabular crystals also appeared. Recrystallization from methyl alcohol gave rectangular plates, arranged in tiers, resembling a roof, the top plate being much smaller than the bottom one and the series forming steps. These melted at 63° .

8. Molecular Weight of Diphenylsulphoneorthocarboxylic Acid.

Determinations of the molecular weight of diphenylsulphoneorthocarboxylic acid, in benzene and in alcohol, gave results as follows:

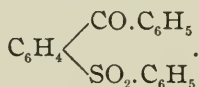
1. 1.2800 grams of the diphenylsulphoneorthocarboxylic acid, dissolved in 38.8300 grams of absolute ethyl alcohol, raised the boiling-point $0^{\circ}.142$ (cor. for barometer), corresponding to a molecular weight of 266.

2. 0.3600 gram diphenylsulphoneorthocarboxylic acid, in 42.8700 grams of anhydrous, thiophene-free benzene, raised the boiling-point $0^{\circ}.082$, corresponding to a molecular weight of 283.

3. 0.8981 gram of the diphenylsulphoneorthocarboxylic acid, dissolved in 42.8700 grams of anhydrous, thiophene-free benzene, raised the boiling-point $0^{\circ}.211$, corresponding to a molecular weight of 275.

The calculated molecular weight of diphenylsulphoneorthocarboxylic acid is 262.

9. *Orthobenzoyldiphenylsulphone,*



This compound was first prepared by Remsen and Saunders,¹ by treating the *s*-orthosulphobenzoic chloride with benzene and aluminum chloride. The mixed chlorides gave the same product.

Canter also obtained the compound in a similar manner from orthophenylsulphonebenzoic chloride (from orthotolylphenylsulphone).

As our acid and chloride are quite different from Canter's, it became of interest to know whether the chloride of the former acid would yield the same product as that of the latter, by the Friedel-Crafts reaction. This was found to be the case.

Twenty grams of the chloride are dissolved in about 250 cc. of benzene and about 25 grams of aluminum chloride added, in portions, at intervals of about 2 hours, the whole operation requiring about 9–10 hours. The flask is heated upon a water-bath and provided with a condenser.

The benzene soon becomes yellowish and fluorescent and this increases as the action proceeds. When hydrochloric acid

¹ THIS JOURNAL, 17, 362.

ceases to be evolved, the contents of the flask, consisting of the dark-colored benzene solution and a tarry mass below, are poured into water. After shaking well and separating the benzene, the water, which becomes milky, is again extracted several times with benzene. The latter is evaporated and the dark-colored residue crystallized from alcohol or benzene. Animal charcoal decolorizes the solution to some extent, but the product was never obtained colorless. It is deposited in flakes and melts at 183° , after several crystallizations.

0.1882 gram substance gave 0.4856 gram CO_2 and 0.0678 gram H_2O .

	Calculated for	
	$\text{C}_6\text{H}_4 \begin{cases} \text{CO} \cdot \text{C}_6\text{H}_5 \\ \text{SO}_2 \cdot \text{C}_6\text{H}_5 \end{cases}$	
C	70.76	Found. 70.36
H	4.39	4.03

Several grams of the substance were fused with potassium hydroxide, in a silver crucible, the temperature being gradually raised to 210° and maintained there for about a half hour. Upon cooling and treating with water the substance partially dissolved, forming a yellowish solution. After filtration and acidification the odor of benzoic acid was at once observed and this, together with potassium chloride, was deposited. It crystallized from alcohol in needles, melting at 120° . The portion insoluble in water was crystallized from alcohol, plates of diphenylsulphone, melting at 124° , being deposited.

IV. OXIDATION OF ORTHOTOLYLPHENYL SULPHIDE.¹

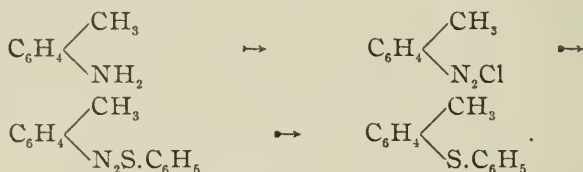
As the acid obtained by Canter had resulted from the oxidation of the methyl group of orthotolylphenylsulphone and diphenylsulphoneorthocarboxylic acid had been formed by the oxidation of the sulphide group of phenylthiosalicylic acid, it was thought possible that, by the simultaneous oxidation of both groups, it might be possible to obtain both products. For this purpose orthotolylphenyl sulphide was prepared by the method of Graebe and Schultess.²

¹ The investigation, up to this point, was conducted by Weedon, in 1902, and repeated by Doughty in 1903-1904. The remainder of the work was done by Doughty.

² *Loc. cit.*

1. *Orthotolylphenyl Sulphide.*

The method employed in the preparation of this compound is entirely analogous to that used for obtaining phenylthio-salicylic acid. The reactions are :



The orthotoluidine, b. p. 195° – 196° , was redistilled twice before using.

Orthotoluidine (31 grams) were mixed with concentrated hydrochloric acid (64 cc.) and water (100 cc.) in a thick-walled beaker, surrounded by crushed ice. To this mixture was added, in small portions, 22 grams of sodium nitrite, dissolved in 100 cc. of water, the temperature being kept below 5° by dropping crushed ice into the beaker. The diazonium solution thus prepared was run, in a thin stream, into a solution of 34 grams of thiophenol and 60 grams of sodium hydroxide in 300 cc. of water, the temperature of this solution being 50° – 60° in order to decompose the diazothiophenol ether as soon as it was formed. A finely-divided, yellow substance was precipitated, which disappeared on stirring and gas was evolved. After all the diazonium solution had been added, the mixture was heated, slowly, on the water-bath until gas evolution ceased. Care must be taken not to heat too rapidly, as the gas may be produced almost explosively. As the heating progressed a heavy, red oil separated. When cool, this was drawn off and dissolved in ether. The solution was dried over fused potassium carbonate and distilled. After removal of the ether the thermometer rose rapidly to 290° and the portion boiling at 290° – 303° was collected. This was redistilled and the fraction boiling at 300° – 305° was separated. According to Graebe and Schultess, pure orthotolylphenyl sulphide boils at $304^\circ.5$. The mercury thermometer used was filled with nitrogen, graduated to 550° and there was no correction for exposed stem.

304.5 mm

Orthotolylphenyl sulphide is a pale yellow, mobile, highly refractive liquid, having a disagreeable odor suggestive of hydrogen sulphide. On long standing it becomes dark reddish-brown.

2. Oxidation of Orthotolylphenyl Sulphide.

Fifteen grams of orthotolylphenyl sulphide were suspended in 2.5 liters of boiling water, contained in a 5-liter round flask, which was heated in a boiling water-bath. Steam was passed into the flask continuously. During the first hour of heating 25 grams of very finely powdered potassium permanganate were added, in small portions. The heating was continued for 16 hours. A few cc. of alcohol were added, to reduce the excess of potassium permanganate, the oxides of manganese were filtered off and the filtrate evaporated to 500 cc. It was then acidified with strong hydrochloric acid. A pale yellowish oil and white crystals were precipitated, the oil becoming solid after standing for some hours. This product was dissolved in hot benzene, from which it crystallized in bunches of short, colorless, radial needles, which melted at 143° (uncor.). When mixed with an equal portion of diphenylsulphoneorthocarboxylic acid, prepared from phenylthiosalicylic acid, the melting-point of the mixture was the same, *viz.*, 143° (uncor.) ; 146° (cor.).

Analysis :

I. 0.3762 gram substance gave 0.8173 gram CO_2 and 0.1316 gram H_2O .

II. 0.2984 gram substance gave 0.6519 gram CO_2 and 0.1065 gram H_2O .

III. 0.3935 gram substance gave 0.3525 gram BaSO_4 (Liebig).

IV. 0.3878 gram substance gave 0.3429 gram BaSO_4 (Liebig).

	Calculated for $\text{C}_6\text{H}_4\begin{matrix} \text{COOH} \\ \text{SO}_2\cdot\text{C}_6\text{H}_5 \end{matrix}$	Found.			
		I.	II.	III.	IV.
C	59.51	59.25	59.57	. .	. .
H	3.85	3.82	3.96	. .	. .
S	12.23	. .	. .	12.05	12.12

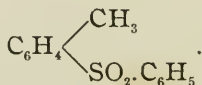
From these results it is evident that diphenylsulphoneorthocarboxylic acid is also formed by the oxidation of orthotolyl-

phenyl sulphide by means of potassium permanganate. No trace of the acid prepared by Canter could be found in the reaction products.

V. "ORTHOPHENYLSULPHONEBENZOIC ACID" (CANTER).

As has been stated, this acid was described by Canter¹ in 1901. He obtained it by oxidizing orthotolylphenylsulphone with potassium permanganate and, from the method of preparation, as well as from the results of analyses, it should have the same formula as the compound we term diphenylsulphone-orthocarboxylic acid. A careful study of the latter having confirmed the correctness of this formula for diphenylsulphone-orthocarboxylic acid, it remained to repeat Canter's work in the hope that some additional light might thus be thrown on the problem.

The orthotolylphenylsulphone used was prepared by Canter's method, from orthotoluenesulphone chloride which remained from Canter's work and was originally supplied by the chemical factory of von Heyden. By treating this with benzene and aluminum chloride, a product was obtained which crystallized from alcohol in white leaflets and melted at 67°.5–68° (uncor.), as stated by him. His analyses accord with the formula



It is soluble in petroleum ether, ordinary ether, benzene, alcohol, glacial acetic acid and in strong nitric acid, from which it is recovered, unchanged, by adding water. This substance will be considered again in another connection.

1. Preparation of "Orthophenylsulphonebenzoic" Acid.

The method described by Canter was followed as closely as possible in the preparation of this substance, the acid obtained melted at 267°, but the yield of pure product was astonishingly small. This was the more surprising as the amount of barium salt, before treating with boiling alcohol, was very

¹ Loc. cit.

considerable and was in fair proportion to the sulphone used, but, after further purification by Canter's method, less than 0.5 gram of the pure acid, melting at 267° , was obtained from 10 grams of sulphone. It was also noticed that the barium salt is completely soluble in boiling alcohol.

Other methods of oxidation were tried, in the hope of increasing the yield. Ammonium persulphate, potassium persulphate, sodium peroxide and chromyl chloride did not effect a satisfactory oxidation. Persulphates destroyed the sulphone entirely. Sodium peroxide had no effect on it, nor had chromyl chloride, in carbon bisulphide solution. The preparation of the acid was, therefore, continued by Canter's method.

By heating the acid, melting at 267° , with lime, diphenylsulphone was obtained, as in the case of diphenylsulphoneorthocarboxylic acid.

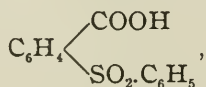
An attempt was made to condense the acid, melting at 260° , to benzophenonesulphone, by heating with concentrated sulphuric acid. After heating the brown, non-fluorescent solution for 14 hours, at 140° , it was cooled and poured into water. A white precipitate formed, which dissolved almost entirely in alkali carbonate or ammonia. When the filter through which this solution had been passed was boiled with alcoholic potassium hydroxide the blue color, characteristic of benzophenonesulphone appeared, fading entirely when the solution cooled. The amount of benzophenonesulphone formed was so small that a less sensitive test than this would hardly have shown its presence. There was not enough to be removed from the filter.

An effort was now made to recover the "unchanged sulphone," which, according to Canter's description, should be found in the alcoholic mother-liquors from the first crystallization of the acid and also in the alcoholic washings from the barium salt. From the former an acid was obtained which did not crystallize from alcohol, but, when the solution was greatly diluted with water, or concentrated by evaporation, it separated as a syrup. It was evaporated to dryness and then it crystallized from benzene in bunches of short, clear, radial needles, melting at 143° (uncor.). A mixture of it with an equal

portion of diphenylsulphoneorthocarboxylic acid had the same melting-point. The washings from the barium salt, referred to above, contained the barium salt of the acid melting at 143° . No orthotolylphenylsulphone was found in either solution. From this it appears that diphenylsulphoneorthocarboxylic acid is formed with the acid described by Canter and a comparison of the quantity of each showed that fully 90 per cent. of the yield is diphenylsulphoneorthocarboxylic acid, which Canter supposed to be "unchanged sulphone." The small yield of Canter's acid is thus fully explained. It is also clear why, after heating this acid with concentrated sulphuric acid, a trace of benzophenonesulphone was found. This suggested a method of purifying Canter's acid; as benzophenonesulphone is insoluble in alkalis, it is easily removed by treating the reaction-product with alkali, filtering the solution of the alkali salt from the insoluble benzophenonesulphone and reprecipitating the acid by hydrochloric acid. An easier and much more satisfactory means of separating the two acids, consists in repeatedly boiling the mixture with fresh portions of water; all of the diphenylsulphoneorthocarboxylic acid is dissolved, while the other acid is not. The acid, melting at 267° , is almost entirely insoluble in boiling benzene, thus giving another means of separation; diphenylsulphoneorthocarboxylic acid easily dissolves in this solvent.

It now remained to ascertain the constitution of the acid melting at 267° . As a preliminary step its molecular weight was determined in alcohol:

1.3230 grams, dissolved in 53.63 grams of absolute ethyl alcohol, gave a rise of $0^{\circ}.108$ in the boiling-point (cor. for bar.) corresponding to a molecular weight of 264.8. This result, together with the formation of diphenylsulphone, by distilling the acid with lime and Canter's analyses of the acid and of its salts, leaves no doubt that its formula is



according to which its molecular weight should be 262.

It is, thererore, isomeric with diphenylsulphoneorothcarboxylic acid, which has been proved to be an ortho compound. Plainly, the acid, melting at 267° , required more careful investigation.

2. Purification of Orthotolyphenylsulphone.

About 40 grams of orthotolyphenylsulphone were prepared as before. In recrystallizing it was found that, if more alcohol was used than was necessary for solution and the crystals which separated first were filtered off and dried, they did not melt at $67^{\circ}.5-68^{\circ}$, but several degrees higher. This indicated the presence of an impurity, hitherto unnoticed, in the product melting at $67^{\circ}.5-68^{\circ}$. Following up this clue, 5-6 fractional recrystallizations, allowing only a small proportion of the substance in solution to separate each time, gave a product which crystallized in beautifully regular, colorless, rhombic plates, which melted sharply at 80° (81° cor.). By this method only a very small quantity of the pure substance was obtained, but, by seeding the solution of material of lower melting-point, with small crystals of the product melting at 80° , a larger portion of the pure compound was separated. The difficulty of purifying it is typical of the tendency, which compounds of this group have, to crystallize in mixtures, having definite melting-points, which remain unchanged by repeated recrystallizations. This particular case is very interesting because the process can be observed under the magnifying glass. The first crystals which appear from a solution of the substance melting at $67^{\circ}.5-68^{\circ}$ are very small, but perfectly shaped, rhombic plates, which move in the solution and rapidly increase in number. After the crystallization has proceeded for a time, however, the points of the diamond-shaped crystals become blunt or rounded. They should be quickly filtered by means of a pump as soon as the slightest sign of this change is seen. If this is done very quickly, the product will be almost pure and melt at nearly 80° . Should the crystallization be allowed to continue and the solution become fairly concentrated, the crystals are irregularly shaped leaflets and melt at $67^{\circ}.5-68^{\circ}$. This, however, is really rather a sharp softening than a true melting, as the

liquid in the tube is not entirely clear and does not lose its cloudiness until a temperature of about 71° is reached, but the change is so sudden and sharp at $67^{\circ}.5$ – 68° that it can very easily be mistaken for a true melting-point. A great number of crystallizations of the substance, melting at $67^{\circ}.5$ – 68° , is necessary in order to prepare even a small proportion of the pure material melting at 80° , and, by actual experiment, 3 weeks' work was required to separate 10 grams of the latter from 40 grams of the former. This is due to the fact that only a very small quantity of the rhombic crystals separate, at each crystallization, before they have to be filtered off and the process repeated.

A few grams of the substance, melting at 80° , were oxidized with potassium permanganate, in the manner already described. The product was solely diphenylsulphoneorthocarboxylic acid, the yield was very satisfactory. This shows that the compound melting at 80° is the true orthotolylphenylsulphone. Not a trace of the acid, melting at 267° , was obtained in this experiment, though very careful search was made for it.

Hence it was evident that Canter's acid, melting at 267° , is not formed from the same sulphone that gives diphenylsulphoneorthocarboxylic acid, but from another, isomeric one, which is present in the product first obtained, melting at $67^{\circ}.5$ – 68° . Considering the difficulty experienced in freeing orthotoluenesulphone chloride from the paratoluenesulphone chloride, which is always formed at the same time and which can only be removed by indirect methods, it seemed probable that the second sulphone might be derived from some paratoluenesulphone chloride, which was present in the, supposedly pure, orthotoluenesulphone chloride used as a starting-point in the preparation of the tolylphenylsulphone, melting at $67^{\circ}.5$ – 68° .

To test this the amide was made from the toluenesulphone chloride used by Canter and ourselves. Crystals melting at 154° – 155° , the melting-point of orthotoluenesulphonamide, were first obtained. From the original ammoniacal filtrate some crystals of orthotoluenesulphonamide also separated. These were removed, the filtrate evaporated to dryness, the residue pulverized, washed on a filter with small portions of

cold water and the slight residue then dissolved in a little hot water. On cooling, white plates separated, which melted at 104° (uncor.). This is known to be one of the melting-points of a mixture of ortho- and paratoluenesulphonamides.¹ When pure orthotoluenesulphonamide and pure paratoluenesulphonamide are mixed in equal proportion, in hot aqueous solution and allowed to crystallize, the product is a mixture, melting generally at 120° or 104° – 108° (uncor.). Intermediate melting-points may be obtained, but recrystallization results in separating the product into two portions, one melting at 120° , the other at 104° – 105° . From these mixtures neither constituent can be separated in a pure condition.

It was evident, therefore, that the orthotoluenesulphone chloride, used by Canter and ourselves, contained some paratoluenesulphone chloride, from which Canter's acid, melting at 267° , was probably derived. The acid in question had been made in this laboratory, by Newell, in 1895, but the melting-point which he gave was 273° , instead of 266° – 267° (Canter) or 267° (ourselves). As Newell states that he used a Zincke thermometer this difference is not surprising, because the other determinations were made with long-stemmed thermometers. However, to avoid any possible confusion on this point, it was decided to make a specimen of paraphenylsulphonebenzoic acid and test its identity by direct comparison with Canter's acid.

VI. PARAPHENYLSULPHONEBENZOIC ACID.

This acid was first prepared by Michael and Adair² from paratolylphenylsulphone, by oxidation with potassium permanganate, in acetic acid solution and also by boiling the sulphone with potassium permanganate, dissolved in a large excess of water. The yield was exceedingly small in each case. The melting-point of their acid was "above 300° ."

In 1895, Newell,² working in this laboratory, investigated the acid. He prepared it by oxidizing paratolylphenylsulphone by means of chromic acid, in glacial acetic acid solution.

¹ Ber. d. chem. Ges., 10, 943. THIS JOURNAL, 1, 170.

² Loc. cit.

He found the melting-point of the acid to be 273° (uncor.), using a Zincke thermometer. The acid was now made by a method analogous to that employed in preparing diphenylsulphoneorthocarboxylic acid. Paraminobenzoic acid was converted into paraphenylsulphidebenzoic acid and this, by oxidation with potassium permanganate, into paraphenylsulphonebenzoic acid.

1. Paraphenylsulphidebenzoic Acid.

A mixture of 40 grams of paraminobenzoic acid, 64 cc. of concentrated hydrochloric acid and 300 cc. of water is cooled to 0° , in a thick-walled beaker, surrounded by crushed ice. A concentrated solution of 22 grams of sodium nitrite is added, in small portions, with stirring, the temperature being kept below 5° by the addition of crushed ice. After the reaction is complete the diazonium solution is run, in a thin stream, from a dropping-funnel, into a solution of 34 grams of thiophenol, 60 grams of sodium hydroxide and 300 cc. of water, which has been heated, in a large beaker, to 50° – 60° . During the addition of the diazonium solution the mixture must be stirred constantly. A light-yellow, curdy precipitate is formed at the point where the diazo solution is added, but this dissolves on stirring, with evolution of gas, forming a dark red solution. This is heated on the water-bath until gas evolution ceases. After cooling, it is acidified with strong hydrochloric acid and paraphenylsulphidebenzoic acid, which is precipitated as a dark red mass, is filtered on a Büchner funnel. The acid is then dissolved in a solution of sodium carbonate, filtered from phenyldisulphide, which is formed by the oxidation of a part of the thiophenol and is again precipitated, by acidifying with strong hydrochloric acid. As thus obtained, the acid is a very impure, red tar, which solidifies on standing. It cannot be purified by crystallization from alcohol, glacial acetic acid, ether or benzene, as the tar is as soluble as the acid in these solvents, nor by making the barium or calcium salt. The only method of purification, which was in the slightest degree satisfactory, was to extract the acid by means of boiling ligroin, using a Soxhlet apparatus and continuing the extraction for days, or even weeks. The

acid is very slightly soluble in ligroin, while the tar is practically insoluble. After the extraction is complete, the ligroin is distilled off and the acid purified by crystallization from alcohol. It is deposited in light, colorless, feathery, elongated, hexagonal plates, which melt at 173° (uncor.); 177° (cor.). The acid thus prepared does not contain water of crystallization. Analysis :

0.1621 gram substance gave 0.1412 gram CO_2 and 0.0625 gram H_2O .

0.2457 gram substance gave 0.2515 gram BaSO_4 .

	Calculated for $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{COOH} \\ \diagup \diagdown \\ \text{S.C}_6\text{H}_5 \end{smallmatrix}$	Found.
C	67.82	67.48
H	4.35	4.27
S	13.91	14.02

The *barium salt* is sparingly soluble in boiling water, from which it crystallizes in very thin plates, containing $2\frac{1}{2}\text{H}_2\text{O}$. Analysis :

0.1113 gram air-dried salt lost 0.0081 gram H_2O when heated to 140° , for 2 hours.

	Calculated for $\left(\text{C}_6\text{H}_4 \begin{smallmatrix} \text{COO} \\ \diagup \diagdown \\ \text{S.C}_6\text{H}_5 \end{smallmatrix} \right)_2\text{Ba} + 2\frac{1}{2}\text{H}_2\text{O}$	Found.
H_2O	7.02	7.27

0.1026 gram dehydrated salt gave 0.0401 gram BaSO_4 .

	Calculated for $\left(\text{C}_6\text{H}_4 \begin{smallmatrix} \text{COO} \\ \diagup \diagdown \\ \text{S.C}_6\text{H}_5 \end{smallmatrix} \right)_2\text{Ba}$	Found.
Ba	23.07	22.98

2. Oxidation of Paraphenylsulphidebenzoic Acid by Means of Potassium Permanganate.

When paraphenylsulphidebenzoic acid is heated with a slight excess of potassium permanganate, in a large quantity of water, paraphenylsulphonebenzoic acid is formed. The method is exactly the same as that already described in the case of oxidizing orthotolylphenylsulphide, but the oxidation

is complete in about 2 hours. The filtrate from the manganese oxides, after evaporation to a small volume, is acidified while hot. If the solution is cold, paraphenylsulphonebenzoic acid is precipitated so finely divided that it is almost impossible to filter it.

Thus obtained the acid is a fine, crystalline, white powder, easily soluble in alcohol, from which it crystallizes in small leaflets melting at 267° (uncor.); 277° (cor.). It is insoluble in benzene and water.

A portion of it was mixed with an equal quantity of the acid, melting at 267° , which had been prepared by Canter's method, from crude orthotolylphenylsulphone, melting at $67^{\circ}.5-68^{\circ}$. The melting-point of the mixture showed no change. From this there can be no doubt that Canter's acid, melting at 267° , is really paraphenylsulphonebenzoic acid and not the ortho compound, as he supposed. Newell found the melting-point of this acid to be 273° (uncor.), using a Zincke thermometer.

The salts described by Canter contain much more water of crystallization than Newell found, but he did not heat them to as high a temperature as Canter used. A sufficient quantity of the acid was not available to permit a thorough examination of all Canter's salts. The barium and calcium salts were made, however and, from their behavior, it seems probable that the figures given by Canter are more nearly correct than Newell's. Neither of these salts loses water of crystallization, to any great extent, at 110° , or even at 130° , but at 165° all of it is easily removed. The salts lose part of their water by standing in a desiccator for several days.

The *barium salt* crystallizes in slender, white needles, containing $3\text{H}_2\text{O}$. Analysis:

0.0839 gram air-dried salt, heated at 165° for $1\frac{1}{2}$ hours, lost 0.0064 gram H_2O .

	Calculated for	Found.
	$\left(\text{C}_6\text{H}_4 \begin{array}{l} \text{COO} \\ \text{SO}_2 \cdot \text{C}_6\text{H}_5 \end{array} \right)_2 \text{Ba} \cdot 3\text{H}_2\text{O}.$	
H_2O	7.57	7.63

I. 0.1467 gram anhydrous salt gave 0.0517 gram BaSO_4 .

II. 0.1770 gram anhydrous salt gave 0.0634 gram BaSO_4 .

	Calculated for $\left(\text{C}_6\text{H}_4 \begin{array}{l} \text{COO} \\ \text{SO}_2 \cdot \text{C}_6\text{H}_5 \end{array} \right)_2 \text{Ba}.$	I.	Found. II.
Ba	20.81	20.79	20.92

The *calcium salt* crystallizes in fine, white needles, containing $6\text{H}_2\text{O}$. Analysis :

0.1817 gram air-dried salt, heated at 165° for $1\frac{1}{2}$ hours, lost 0.0294 gram H_2O .

	Calculated for $\left(\text{C}_6\text{H}_4 \begin{array}{l} \text{COO} \\ \text{SO}_2 \cdot \text{C}_6\text{H}_5 \end{array} \right)_2 \text{Ca} \cdot 6\text{H}_2\text{O}.$	Found.
H_2O	16.14	16.18

I. 0.1525 gram anhydrous salt gave 0.0365 gram CaSO_4 .

II. 0.1030 gram anhydrous salt gave 0.0247 gram CaSO_4 .

	Calculated for $\left(\text{C}_6\text{H}_4 \begin{array}{l} \text{COO} \\ \text{SO}_2 \cdot \text{C}_6\text{H}_5 \end{array} \right)_2 \text{Ca}.$	I.	Found. II.
Ca	7.11	7.04	7.06

Though there now remained no doubt as to the identity of Canter's acid, the melting-points found by him for the chloride and amide differ so much from those given by Newell that it was thought necessary to examine these compounds. In the experiments made to determine this question, the acid employed had been prepared by Canter's method, but that used in preparing the salts described above was made by oxidizing parphenylsulphidebenzoic acid.

3. Paraphenylsulphonebenzoic Chloride.

The acid was mixed with a little more than its own weight of phosphorus pentachloride, in a small flask, which was immersed in a sulphuric acid-bath. The temperature of the bath was raised gradually to 200° . No action at all could be detected until a temperature of 125° was reached and it did not become at all vigorous until 140° . At this temperature the mass melted and hydrochloric acid was evolved freely. According to Canter the reaction begins at ordinary temperatures and proceeds rapidly when the flask is heated at 45° . After heating at 200° for an hour the product was poured into a

dish, it solidified to a light-brown, crystalline mass. This was powdered and washed with water at 40° , first by decantation and then on a filter, with suction. By this treatment it became almost white; it was then dried, dissolved in boiling ligroin, in which it is sparingly soluble and from which it crystallized in small, colorless, square plates. After several recrystallizations it melted at 143° – 144° (uncor.); 146° – 147° (cor.). Newell found $145^{\circ}.2$ – $145^{\circ}.8$, using a Zincke thermometer. Canter crystallized it from glacial acetic acid and gives its melting-point at $162^{\circ}.5$ – $263^{\circ}.5$.

4. *Paraphenyldisulphonebenzamide.*

A portion of paraphenyldisulphonebenzoic chloride, prepared as above, was digested with a large excess of concentrated ammonia, for 24 hours, at the ordinary temperature. The insoluble product was filtered, washed with cold water and then dissolved in boiling water, in which it is rather sparingly soluble. On cooling, feathery, white crystals separated, which melted at 240° – $240^{\circ}.5$ (uncor.); $248^{\circ}.3$ – $248^{\circ}.8$ (cor). Newell gives 242° – 243° , using a Zincke thermometer; Canter gives 254° – 255° .

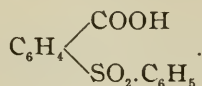
Conclusions.

The results of this investigation may be summarized as follows:

1. When phenylthiosalicylic acid is oxidized with dilute nitric acid, the product of the reaction is almost entirely diphenylsulphoxideorthocarboxylic acid.

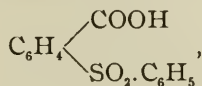
2. When phenylthiosalicylic acid is treated with fuming nitric acid, a substance is obtained having the melting-point of the acid described by Graebe and Schultess. It is a mixture of diphenylsulphoxideorthocarboxylic acid and a mononitro derivative of this acid. The proportion of the nitro compound is increased by heating a solution of phenylthiosalicylic acid in fuming nitric acid.

3. When phenylthiosalicylic acid is oxidized by means of potassium permanganate, diphenylsulphoneorthocarboxylic acid is formed. The reactions of this acid show it to have the formula,



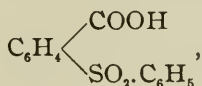
4. When orthotolylphenylsulphide is oxidized by means of potassium permanganate, diphenylsulphoneorthocarboxylic acid is produced.

5. The acid melting at 267° , obtained by Canter and supposed, by him, to be orthophenylsulphonebenzoic acid,



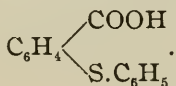
is really the isomeric paraphenylsulphonebenzoic acid, which had been made previously by Newell. Its formation, under the conditions of Canter's investigation, was due to the presence of paratoluenesulphone chloride in the orthotoluenesulphone chloride with which he worked.

6. When pure orthotolylphenylsulphoné is oxidized with potassium permanganate, diphenylsulphoneorthocarboxylic acid,



is the only product obtained.

7. Paraphenylsulphidebenzoic acid is produced from paraminobenzoic acid and thiophenol, by a process exactly analogous to that of phenylthiosalicylic acid from anthranilic acid and thiophenol. Paraphenylsulphidebenzoic acid is oxidized to paraphenylsulphonebenzoic acid (diphenylsulphoneparacarboxylic acid) by means of potassium permanganate, just as phenylthiosalicylic acid is oxidized to diphenylsulphoneorthocarboxylic acid under similar conditions. This reaction, together with analyses of the acid and its barium salt, show the formula of paraphenylsulphidebenzoic acid to be



This investigation was suggested to us by President Remsen and was conducted under his supervision. We desire to express our thanks and obligations to him.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, MD.,
June, 1904.

NOTE.

On the Change of Concentration of Solutions and on the Crystallization of Dissolved Substances under the Influence of Centrifugal Force.

A paper bearing the above title has recently appeared.¹ It contains an account of some interesting and important experiments by van Calcar and Lobry de Bruyn. A homogeneous solution was placed in a vessel, which was rapidly rotated. The rotation was continued for $1\frac{1}{2}$ –3 hours, at a rate of about 2400 turns per minute. On removing samples of the solution from different portions of the vessel and analyzing them, it was found that the solution was no longer homogeneous, but became more and more concentrated as the distance from the center of the vessel increased. The greatest concentration, however, was not found at the very periphery of the vessel, as would be expected, but some little distance from it. This was shown to be due to a lessening of the speed of rotation when the samples were removed for analysis.

A saturated solution of sodium sulphate was then rotated for 5 hours, at about the same rate, *i. e.*, about 2400 turns per minute. The salt crystallized out of the solution, around the periphery of the vessel, until the solution, which originally contained 8.78 per cent of the salt, showed, on analysis, only 5.54 per cent.

The authors have calculated the magnitude of the force acting on the solution, under the above conditions and have shown that, at the periphery, it is about 400,000 dynes.

The cause of all diffusion in solutions is osmotic pressure. Were it not for osmotic pressure no solution would remain homogeneous for any appreciable time, unless the dissolved substances happened to have the same specific gravity as the solvent. If osmotic pressure did not exist the dissolved substance would fall to the bottom of the solution if it were heavier than the solvent; if lighter it would rise to the top.

The experiments above described are really important as furnishing a mechanical means of partially overcoming os-

¹ Rec. Trav. Chim., 23, 218 (1904).

motie pressure. By the great centrifugal force produced by the high velocity, the dissolved substance is driven through the solvent out towards the periphery, accumulates there and makes the solution more concentrated in this region. It will be seen that this is acting directly against osmotic pressure, which always drives the dissolved substance in that direction which is necessary to establish or maintain homogeneity of concentration.

This suggests, in a way, the "Principle of Soret," where homogeneity is destroyed by keeping the different parts of the solution at different temperatures.

H. C. J.

OBITUARY.

ALBERT BENJAMIN PRESCOTT.

Dr. Albert B. Prescott was born at Hastings, N. Y., Dec. 12, 1832, and died at Ann Arbor, Mich., Feb. 26, 1905, in his seventy-third year. The whole of his active life was spent in connection with the University of Michigan, from which he graduated M.D., 1864; Ph.D., 1886; LL.D., 1896. He also received the LL.D. from Northwestern University, in 1903. He had been professor of Organic and Applied Chemistry since 1870, dean of the School of Pharmacy since 1876 and director of the Chemical Laboratory since 1884. In 1891 he was president of the American Association for the Advancement of Science, president of the American Pharmaceutical Association, 1900, and a member of various chemical and pharmaceutical societies in this country and abroad. Dr. Prescott's contributions to scientific knowledge chiefly related to analysis and pharmacy, several of his papers were contributed to the earlier volumes of *THIS JOURNAL* and he was the author of a number of text-books on qualitative and organic analysis. As a successful teacher Dr. Prescott was widely known and highly esteemed; his interest in research was always keen and he was constantly seeking opportunities to assist, in every possible way, the younger men who showed ability in this direction.

REVIEWS.

EXPERIMENTS ARRANGED FOR STUDENTS IN GENERAL CHEMISTRY. By EDGAR F. SMITH, Professor of Chemistry, University of Pennsylvania, and HARRY F. KELLER, Professor of Chemistry, Central High School of Philadelphia. Fifth edition. Philadelphia: P. Blakiston's Son & Co. 1904.

This little book is an excellent laboratory manual for those

beginners who use a text-book which does not give directions for laboratory experiments.

E. R.

MANUAL OF PHYSIOLOGICAL AND CLINICAL CHEMISTRY. By ELIAS H. BARTLEY, B.S., M.D., PH.G., Professor of Chemistry, Toxicology and Pediatrics in the Long Island College Hospital. Second edition. Philadelphia: P. Blakiston's Son & Co. 1904. pp. 188.

This carefully prepared little manual is well adapted to the purpose for which it was intended, namely, such medical courses that allot but the minimal time to chemistry. A small part is devoted to general physiological chemistry, then the chemistry of the urine, gastric contents, faeces and milk are taken up in detail and in a very satisfactory way, considering the limited space. The examination of urinary and biliary calculi is also discussed. Brief accounts of the clinical significance of the work are given at the ends of the chapters. The author also enters into the microscopical findings. For those medical courses, where the time devoted to physiological and clinical chemistry is limited, this little volume is to be recommended.

A. S. L.

LES NOUVEAUTÉS CHIMIQUES POUR 1904. By CAMILLE POULENC. Paris: J. P. Baillièrre et Fils. 1904. pp. viii + 352. Price, 4 Fr.

The title of this book is somewhat misleading, as the preface is dated April, 1904 and, consequently, the subjects discussed are older than might be expected. The contents of the five chapters are as follows: (I.) Apparatus for the determination of physical properties, such as high temperatures, density, refractive index, etc. A good description of Olszewski's apparatus for the liquefaction of gases is given. (II.) Chemical apparatus in the more restricted sense; this includes appliances for distillation and for the preparation and purification of gases. (III.) Electrical apparatus. (IV.) Analytical apparatus. (V.) Apparatus chiefly used by bacteriologists. The descriptions, in general, are clear, full references being made to their sources; the text is illustrated by 185 figures. The selection of subjects appears to be good, in so far as the author has availed himself of scientific literature, but his self-imposed limitations are curious and will be apparent when it is stated that, of journals in the English language, he cites only the "Chemical News," once! German publications fare better, because reference is made, somewhat freely, to the "Chemiker-Zeitung" and to "Eisen und Stahl." That this action on the part of the author constitutes an injustice to the activity of English-speaking chemists is, perhaps, of minor importance, it also greatly detracts from the value of the book which, other-

wise, is interesting and should prove useful. A good index is provided.

J. B. T.

THE URINE AND THE CLINICAL CHEMISTRY OF THE GASTRIC CONTENTS, THE COMMON POISONS AND MILK. By J. W. HOLLAND, M.D., Professor of Medical Chemistry and Toxicology, Jefferson Medical College of Philadelphia. Seventh edition. Philadelphia: P. Blakiston's Son & Co. 1904. pp. 172.

The book is, apparently, intended for the author's own course as a laboratory manual and is interleaved with blank pages for the student to utilize in taking notes. The directions for the experiments are quite clear, but the metric system is not used throughout. The theoretical remarks contain too many mistakes and inaccuracies to be enumerated here.

A. S. L.

INTRODUCTION TO CHEMICAL ANALYSIS FOR BEGINNERS. From the Tenth German Edition of PROF. DR. FR. RÜDORFF, Professor of Chemistry in the Technical High School, Charlottenburg, Berlin, Prussia. Authorized translation by PROF. CHAS. B. GIBSON, M.D. Chicago: Chicago Medical Book Co. 1902.

Prof. Rüdorff—to quote his preface—has endeavored to set forth the principles of analytical chemistry with a limited number of elements and their more important compounds. This method has been well received in Germany and is to be recommended, where the time devoted to chemistry by the student is brief, as in high schools and medical and dental colleges.

E. R.

JAHRBUCH DER CHEMIE. Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie. Unter Mitwirkung von H. BECKURTS, Braunschweig, C. A. BISCHOFF, Riga, G. BODLÄNDER, Braunschweig, M. DELBRÜCK, Berlin, J. M. EDER, Wien, TH. FISCHER, Berlin, P. FRIEDLÄNDER, Wien, C. HÄUSSERMANN, Stuttgart, A. HERZFELD, Berlin, W. KÜSTER, Tübingen, J. LEWKOWITSCH, London, A. MORGEN, Hohenheim, F. QUINCKE, Leverkusen, A. WERNER, Zürich. Herausgegeben von RICHARD MEYER, Braunschweig. XIII Jahrgang, 1903. Druck und Verlag von Friedrich Vieweg und Sohn. 1904.

This annual visitor gives the usual pleasure and satisfaction. Every working chemist will welcome it and feel the better for its coming. From the preface we learn that Professor F. W. Küster has been obliged to withdraw from the staff and that Professor Bodländer has taken the place thus left vacant and has prepared the report on Physical Chemistry. Professor Doelz has also resigned and Dr. Th. Fischer, of Berlin, has prepared the report on Mining. Further, the editor, Professor Richard Meyer, has been prevented from furnishing his usual report on the Chemistry of Tar and Dyes and Professor F. Friedländer has prepared the report on this subject for this volume.

In the report on Physical Chemistry there is a most appreciative note on J. Willard Gibbs from which the following is quoted: "Gibbs war Mathematiker oder mathematischer Physiker und hat trotzdem für die Chemie das Grösste geleistet. Er hat die chemischen Erscheinungen mit den Aesserungen der anderen Energieformen in Zusammenhang gebracht und insbesondere die Beziehungen der chemischen Energie zur Wärme aufgeheilt. Es war durch seine Untersuchungen möglich, für die chemische Verwandtschaft ein genaues Mass zu finden wodurch auch die Elektrochemie einen wichtigen Fortschritt erfahren hat. * * * Während auf den übrigen Gebieten einzelne Resultate, zu denen Gibbs gelangt war, schon vor ihm oder unabhängig von ihm von anderen gefunden worden sind, ist die Phasenregel ausschliesslich auf Gibbs zurückzuführen. Sie allein würde dem Mathematiker für immer einen hervorragenden Platz unter den ersten chemischen Forschern sichern."

Under Physical Chemistry there is a section devoted to Radio-activity and under Inorganic Chemistry another section, of five pages, treats of Radio-active Substances. These brief and clear summaries will be a relief to those who have been overwhelmed by the numerous articles on the subject of radio-activity that have appeared in so many different journals.

We are informed that the amount of artificial indigo in use is constantly increasing, being now about equal to that of the natural product. The larger dye works in Germany, Austria and the United States use synthetical indigo almost exclusively.

But only a careful examination of the book can make clear its value.

I. R.

DIE HETEROGENEN GLEICHGEWICHTE VOM STANDPUNKTE DER PHASEN-LEHRE. Von DR. H. W. BAKHUIS ROOZEBOOM, Professor an der Universität Amsterdam. Zweites Heft, Systeme aus zwei Komponenten. Erster Teil, mit 149 eingedruckten Abbildungen und zwei Tafeln. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1904. pp. 467. Price, M. 12.50.

The appearance of the first *Heft* of this work has already been noticed.¹ It only remains to call attention to the appearance of the second one, which deals with heterogeneous equilibria in binary systems. "It contains a complete survey of the equilibria between solid, liquid and gaseous phases, of such binary mixtures where only the components appear as solid phases." This second part seems to be of the same high character as the first.

H. C. J.

¹ THIS JOURNAL, 27, 78.

MANUAL OF THE CHEMICAL ANALYSIS OF ROCKS. By HENRY S. WASHINGTON, PH.D. First edition. New York : John Wiley & Sons. 1904. pp. ix + 183.

This manual is designed to furnish "to chemists, petrologists, mining engineers and others who have not made a particular study of quantitative analysis, a selection of methods for the chemical analysis of silicate rocks, especially those of igneous origin." It is assumed that the reader's previous experience has probably been limited to the conventional analysis of a feldspar, hence, the methods given are described in great detail and are said to be approved by the chemists of the U. S. Geological Survey and by the author. Although they have been selected with special reference to igneous silicate rocks, they may be applied to metaphoric and sedimentary silicate rocks as well; but they are not, in general, applicable to the analysis of ores. Considerable care is also taken to point out the significance of the results of chemical analysis, in furthering the objects sought in the science of petrology.

The text is divided into four parts, designated, respectively, as follows: Introduction; Apparatus and Reagents; The Sample; Methods. An appendix contains some specimen calculations of analyses, a table of molecular weights of some twenty of the commonly used oxides, together with the atomic (not molecular) weights of sulphur, chlorine and fluorine and a short table of factors.

Under "Methods" are included procedures for the determination of each of the common constituents of silicates and also of nickel, titanium, barium, zirconium, chromium, vanadium, copper, fluorine, chlorine, sulphur and carbon dioxide. The chief sources of error, the extent of allowable errors and economy of time are all discussed at length.

For the petrologist, with little time to devote to the critical study of methods or the acquisition of technical skill in analysis, the author's efforts to supply a useful handbook may fairly be regarded as successful, provided consideration is given to the limitations, which necessarily, because of inexperience, attach to the powers of observation of such an analyst. The procedures are given in such painstaking detail that results are safe-guarded, as far as a text-book may effect this end; but, when the possibilities of unexpected complications are so great as in a rock analysis, a relatively untrained analyst can hardly hope to obtain results which are above suspicion. Skill will, however, gradually follow practice and the path to success is well-blazed in this work; the analyses completed, meanwhile, may be of assistance, even though they may not be of scientific accuracy.

The author has, in his desire to enforce his ideas, allowed himself to duplicate statements, under different headings, to a degree which sometimes tends to test the patience of the reader, in spite of the laudable purpose in the background. The index is unusually complete.

H. P. TALBOT.

TABLES FOR QUALITATIVE CHEMICAL ANALYSIS, Arranged for the Use of Students, by A. LIVERSIDGE, M.A., LL.D., F.R.S., Professor of Chemistry in the University of Sydney. Second edition. London: Macmillan. 1904.

This brief manual differs from the majority of others of the same length, by including the reactions of most of the rare elements and those of many organic compounds, particularly the substances interesting to medical students. The book is concise and clearly worded.

E. R.

ELECTRO-CHEMISTRY. Part I., General Theory. By R. A. LEHFELDT, D.Sc., Professor of Physics at the East London Technical College, including a chapter on the "Relation of Chemical Constitution to Conductivity," by T. S. MOORE, B.A., B.Sc., Lecturer in the University of Birmingham. London, New York and Bombay: Longmans, Green & Co. 1904. pp. 268 Price, \$1.60.

This work, we regret to say, falls very far behind Findlay's Phase Rule in both the selection and arrangement of material. In the selection of material much that is fundamental has been omitted entirely and there is a general lack of perspective in the treatment of the matter that is included in the book. One fails to find clean-cut, succinct statements about the most important matters, which are so essential to a student just entering the field.

Again, we object to the use of symbols for the names of chemical compounds. For example: p. 40, "filled with NaCl solution;" p. 41, "with solutions of K_2SO_4 , $BaCl_2$ and BaN_2O_6 ;" p. 41, "that of the K_2SO_4 solution used," do not sound well, and would scarcely pass as good English.

The book does undoubtedly contain much valuable material and can be profitably read by any one except a beginner in electrochemistry; but for several reasons, a few of which are here pointed out, the work does not seem to be adapted to the needs of one just commencing the study of this chapter of physical chemistry.

H. C. J.

AMERICAN CHEMICAL JOURNAL

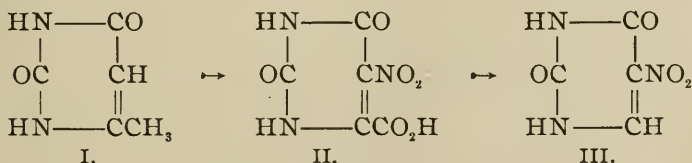
Contributions from the Sheffield Laboratory of Yale University.

CXXII. — RESEARCHES ON PYRIMIDINES: THE STRUCTURE OF SOME SUBSTITUTION- PRODUCTS.

[EIGHTH PAPER.]

BY HENRY L. WHEELER AND H. STANLEY BRISTOL.

When a pyrimidine derivative, having hydrogen both in the 4- and 5-positions, is attacked by the halogens or nitric acid, the question as to which hydrogen atom is replaced or substituted has not, hitherto, been decided. A method, which has now been successful in dealing with this question, depends on the structure of Behrend's nitro- and aminouracil. Nitro-uracil has the nitro group in the 5-position, as it is prepared from 4-methyluracil,¹ (I.), or 5-nitrouracil-4-carboxylic acid², (II.):



¹ Kohler: *Ann. Chem. (Liebig)*, **236**, 50 (1886).

² Behrend: *Ibid.*, **229**, 36 (1885); **240**, 5 (1887).

Aminouracil results by reduction of the above nitrouracil, the amino group is, therefore, in the 5-position. Neither nitrouracil nor aminouracil has a definite melting or decomposing point. 5-Aminouracil picrate, however, has a definite effervescing point, which serves to identify it. Behrend and Grünwald¹ state that this compound melts at 147°-148°. This is incorrect, possibly a typographical error. It has been found, by several workers in this laboratory, that the action of nitric acid on uracil, 2-ethylmercapto-6-oxypyrimidine, 2-thiouracil and other pyrimidine derivatives leads to the formation of a nitrouracil. In each case, after reduction with aluminium amalgam, the product gave a picrate effervescing sharply at 247°, or 100° higher than the temperature given by the above authors. At the request of one of us, Mr. C. O. Johns prepared 5-nitrouracil (III.) by Behrends' method and this, on reduction, gave a picrate showing no signs of melting at 147° but effervesced, as in the other cases, at 247°. The compounds were identical and it therefore follows that nitric acid attacks these various pyrimidine derivatives in the 5-position.

For the purpose of comparison, Traube's 2,6-dioxy-4-aminopyrimidine or 4-aminouracil² was prepared. When the saturated aqueous solution of this substance was mixed with a saturated solution of picric acid no precipitate resulted and no picrate was obtained.

It was stated in a previous article³ that Dr. Merriam obtained 5-aminouracil when the product, obtained by brominating uracil, was heated with aqueous ammonia at 180°; it was identified by means of its picrate. A specimen of the picrate, prepared by Dr. Merriam, was found, by us, to sinter decidedly about 147°, but did not melt, or rather effervesce, until 247°. The compound proved to be identical with the above products and it therefore follows that bromine attacks uracil in the 5-position, as previously represented.

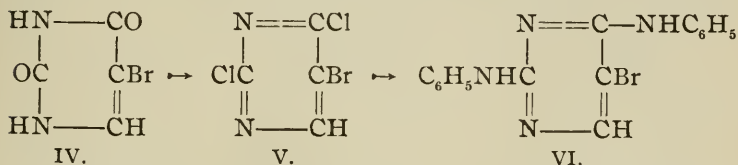
It might be expected that a 2-alkylmercapto-6-oxypyrimidine would also give a 5-brom derivative. This was proved to be the case as follows: 5-Bromuracil (IV.) was converted into

¹ Ann. Chem. (Liebig), **309**, 259 (1899).

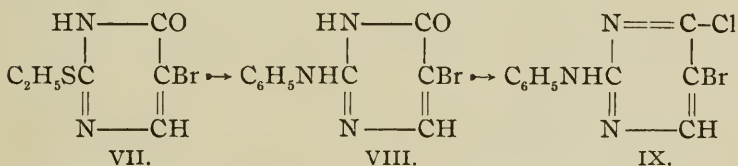
² Ber. d. chem. Ges., **33**, 1381 (1900).

³ THIS JOURNAL, **31**, 603 (1904).

2,6-dichlor-5-brompyrimidine (V.) by warming with a mixture of phosphorus oxychloride and phosphorus pentachloride and this, with aniline, gave 2,6-dianilino-5-brompyrimidine (VI.) :



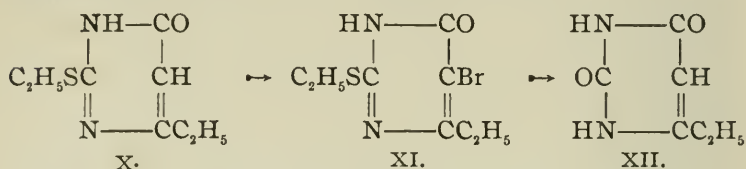
2-Ethylmercapto-6-oxypyrimidine was treated with bromine, in glacial acetic acid and the resulting brom derivative (VII.) was warmed with aniline ; this gave 2-anilino-5-brom-6-oxypyrimidine (VIII.), which was then converted into the chloride (IX.). When this chloride was warmed with aniline the product was found to be identical with the above dianilino-brompyrimidine (VI.), so that the process can be represented as follows :



Our first plan of procedure for deciding the question of the position of bromine in the mercaptooxypyrimidines, was to boil these products with hydrochloric acid and identify the brom-uracil formed. It was found, however, that prolonged boiling of 2-ethylmercapto-5-brom-6-oxypyrimidine with hydrochloric acid gave uracil, the bromine being entirely removed. The 5-brom derivatives of uracil part with their halogen more readily than those of cytosine or, in other words, an oxygen in the 6-position renders bromine in the 5-position more active than when the 6-position is occupied by an amino group. This is true not only for the replacement of bromine by hydrogen, but also by the amino group.

We have found that 2-ethylmercapto-4-ethyl-5-brom-6-oxypyrimidine (XI.) also loses bromine by simply evaporating its solution, in concentrated hydrochloric acid, to dryness on the

water-bath, the product obtained being 4-ethyluracil (XII.). The 2-ethylmercapto-4-ethyl-6-oxypyrimidine (X.) for this experiment was prepared by the condensation of the ethyl bromide addition-product of thiourea and ethylpropionylacetate, $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CO}.\text{OC}_2\text{H}_5$,¹ in alkaline solution.



Bromine is represented in XI. as entering at the 5-position and not in the alkyl group. Behrend² has shown that when 4-methyluracil is brominated and then oxidized bromuracil-carboxylic acid results.

EXPERIMENTAL.

The uracil used in this work was prepared by boiling various 2-alkylmercapto-6-oxypyrimidines with concentrated hydrochloric acid. In the course of our experiments a number of new pseudoureas and alkylmercapto pyrimidines were employed. The former were prepared, for analysis, by treating pure, finely-powdered thiourea with a little alcohol and the alkyl halide was added. The mixtures were warmed on the steam-bath until solution took place and allowed to crystallize, in a vacuum, over sulphuric acid. The crystals were then simply washed with ether; they were readily soluble in water and alcohol and insoluble in benzene and ether. It was found that pseudoethylthiourea hydrobromide dissolved in acetone, it was readily soluble in pyridine and it could be crystallized from acetic anhydride.

Pseudonormalpropylthiourea hydrobromide formed long, colorless needles, which melted at about 60°.

	Calculated for $\text{C}_4\text{H}_{14}\text{N}_2\text{S}.\text{HBr}.$	Found.
N	14.07	14.19

Pseudoisobutylthiourea hydrobromide formed a fibrous mass of crystals, melting at about 96°.

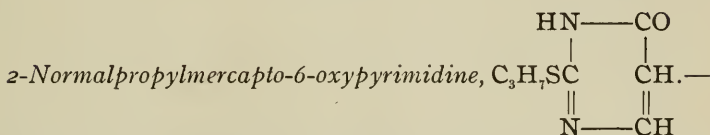
¹ Blaise : Compt. rend., 132, 978 (1901).

² Ann. Chem. (Liebig), 240, 22 (1887).

	Calculated for $C_6H_{12}N_2S.HBr.$	Found.
N	13.14	13.21

Pseudoisoamylthiourea hydrobromide crystallized in long prisms, melting at about 84° .

	Calculated for $C_6H_{14}N_2S.HBr.$	Found.
N	12.33	12.28



This and the following alkylmercaptopyrimidines were prepared by the method described in the case of the corresponding ethyl derivative.¹ The product from the condensation of 20 grams of the normalpropylbromide addition-product of thiourea, 30 grams of ethyl sodium formylacetate and 6 grams of sodium hydroxide, amounted to 12 grams. It was readily soluble in alcohol and hot water. From 40 per cent alcohol it formed long, colorless needles, melting at 117° .

	Calculated for $C_7H_{10}ON_2S.$	Found.
N	16.47	16.39

2-Isobutylmercapto-6-oxy pyrimidine.—Twenty-one grams of the above pseudoisobutylthiourea hydrobromide, 38 grams of ethyl sodium formyl acetate and 4 grams of sodium hydroxide gave about 12 grams of this mercaptopyrimidine. When crystallized from 50 per cent alcohol it formed leaf-like plates, melting at 107° .

	Calculated for $C_8H_{12}ON_2S.$	Found.
N	15.21	15.19

2-Isoamylmercapto-6-oxy pyrimidine crystallized from 50 per cent alcohol in long, thin plates, melting at 115° .

	Calculated for $C_9H_{14}ON_2S.$	Found.
N	14.14	14.08

Nitration of Uracil (By Mr. S. H. Clapp).—One gram of uracil was added to a mixture of 5 cc. of concentrated sul-

¹ THIS JOURNAL, 29, 483 (1903).

phuric acid and 10 cc. of fuming nitric acid. The mixture was heated to about 125° , in an oil-bath, for an hour. On pouring into ice-water, nitrouracil separated in colorless, prismatic needles. The yield was about 1 gram. This compound was reduced by means of aluminium amalgam, in ammoniacal solution. On filtering and concentrating, aminouracil separated in balls of needles, which were recrystallized from water; they gave 33.47 per cent of nitrogen, the calculated being 33.07.

5-Aminouracil Picrate.—The above aminouracil was dissolved in warm water and a hot solution of picric acid was added, the picrate then separated in the form of yellow, rectangular plates which began to sinter strongly at 150° , then melted, with effervescence, at 247° – 248° .

	Calculated for $C_{10}H_8O_9N_5$.	Found.
N	23.59	23.27

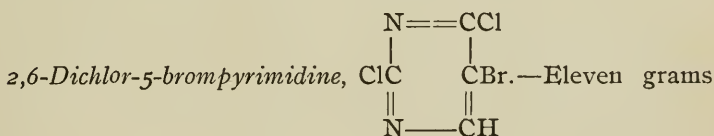
Nitration of 2-Ethylmercapto-6-oxypyrimidine.—2-Ethylmercapto-6-oxypyrimidine can be dissolved in a mixture of fuming nitric acid and concentrated sulphuric acid, at the ordinary temperature and be recovered, unaltered, on pouring into ice-water and neutralizing with sodium carbonate. If the mixture is warmed on the steam-bath until the reaction is well started, then allowed to stand in a warm place (about 60°), large crystals of nitrouracil separate.

The following was found to be the easiest method of preparing nitrouracil: Ten grams of 2-ethylmercapto-6-oxypyrimidine were dissolved in a mixture of 20 cc. of red, fuming nitric acid, 10 cc. of concentrated nitric acid and 10 cc. of concentrated sulphuric acid. The reaction was started by warming on the steam-bath, then the liquid was allowed to stand, at about 60° , for several hours, 4.9 grams of well-crystallized nitrouracil separated. The crystals were filtered and the acid filtrate allowed to stand for 24 hours longer, at 60° , whereupon 2.7 grams of nitrouracil separated, or 7.6 grams in all. This is a yield of 75.5 per cent of the calculated. When the compound was reduced by means of aluminium amalgam and the picrate prepared, it was found that the latter became

black at about 190°, but nevertheless effervesced sharply at 247°. The same partial decomposition and effervescing point was noticed in the case of the picrate prepared in the following experiment.

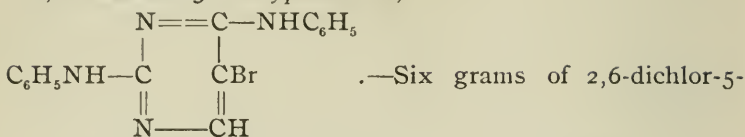
Nitration of 2-Thio-6-oxypyrimidine.—Twenty-five per cent nitric acid reacts energetically with this pyrimidine derivative and a portion is converted into nitrouracil. Eight grams of 2-thiouracil gave about 4 grams nitrouracil; beside this a far more soluble substance was formed, which gave a bulky precipitate with mercuric chloride, it was probably 6-oxypyrimidine, but was not isolated.

Nitration of 2-Ethylmercapto-6-chlorpyrimidine (By Dr. T. B. Johnson).—The mercaptochlorpyrimidine (1.5 grams) was added to a mixture of 4 cc. of concentrated nitric acid and 4 cc. of concentrated sulphuric acid. The temperature of the mixture was not allowed to rise above 90°; it was maintained at this point until effervescence ceased. The product was cooled, poured on to ice and crystallized from water; it contained 27.1 per cent nitrogen, the calculated percentage for nitrouracil is 26.7. This substance was reduced and the picrate prepared; it melted or effervesced at 247°.



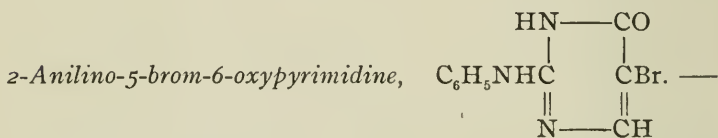
of 5-bromuracil, 13 grams of phosphorus pentachloride and 40 cc. of phosphorus oxychloride were mixed and warmed on the steam-bath. Hydrogen chloride was evolved and, after 4 days, all of the bromuracil dissolved. The solution was poured on to ice and extracted with ether. The ether was dried over calcium chloride and evaporated, leaving 8 grams of oil, which boiled at 119°–120° (17–18 mm.). It solidified, in a freezing-mixture, to a crystalline mass and melted at –3° – –2°.

	Calculated for C ₄ HN ₂ Cl ₂ Br.	Found.
N	12.28	12.46

2,6-Dianilino-5-bromypyrimidine,

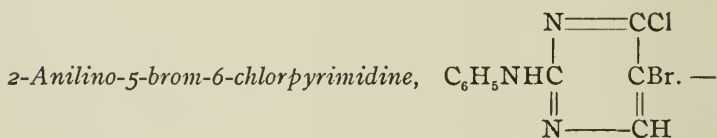
bromypyrimidine were mixed with 10 grams of aniline, heat was evolved and the mass solidified to a hard cake. This was powdered and boiled with benzene, the benzene and aniline were removed by a current of steam and the insoluble material was crystallized from alcohol. It formed a felted mass of colorless needles, difficultly soluble in water, which melted to a clear oil at 191° .

	Calculated for $\text{C}_{16}\text{H}_{13}\text{N}_4\text{Br}$.	Found.
N	16.42	16.42



Five grams of 2-ethylmercapto-5-brom-6-oxypyrimidine were heated with excess of aniline on the steam-bath, until the odor of mercaptan disappeared (24 hours). At first solution took place, then crystalline material separated. The product, after washing with cold alcohol, was free from sulphur and weighed about 6 grams. It was difficultly soluble in water, alcohol, benzene and acetone. From alcohol it separated in the form of colorless, needle-like prisms, melting at 246° with effervescence.

	Calculated for $\text{C}_{10}\text{H}_8\text{ON}_3\text{Br}$.	Found.
N	15.78	16.11

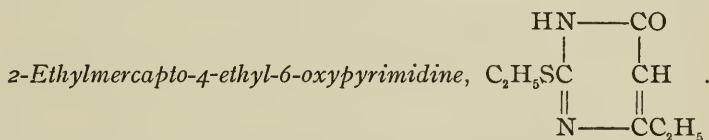


The above anilinobromoxypyrimidine (4.7 grams) was digested on the steam-bath with phosphorus oxychloride until solution took place and hydrogen chloride ceased being

evolved. It was then poured on to ice and the solid that separated was extracted with ether. It was readily soluble in ether and benzene and crystallized from ligroin in bunches of long, radiating, colorless needles which melted, to a clear oil, at 106° – 107° .

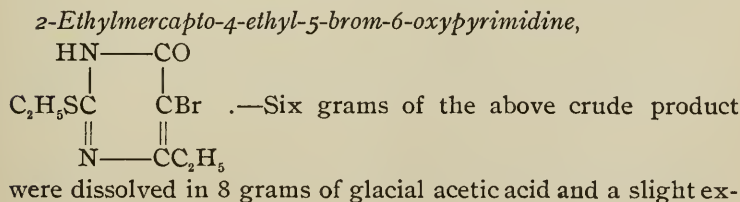
	Calculated for $C_{10}H_7N_3ClBr$.	Found.
N	14.76	14.45

A small quantity of this compound was warmed with excess of aniline on the steam-bath, the mixture liquefied and in a few minutes solidified to a hard cake. On crystallizing from alcohol it gave a felted mass of needles, melting at 191° and, when mixed with 2,6-dianilino-5-brompyrimidine, described above, the melting-point was not altered.



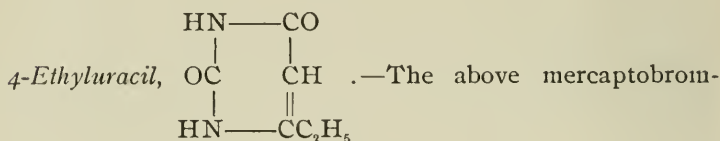
—A solution of 5.7 grams of sodium hydroxide, 12.5 grams of pseudoethylthiourea hydrobromide and 10 grams of ethyl propionyl acetate was made in 25 cc. of water, the constituents being added in the order named. The mixture was allowed to stand for a number of hours, then warmed and, on cooling, it was acidified with acetic acid. An oil separated which finally solidified, and, after washing and drying, weighed about 6 grams. It dissolved, with difficulty, in hot water, giving colorless, truncated pyramids. From alcohol, in which it is very soluble, it crystallized in large, stout, transparent prisms, which melted at 89° without decomposition.

	Calculated for $C_8H_{12}ON_2S$.	Found.
N	15.21	15.13



cess of bromine added. A mass of six-sided plates separated and more was obtained on diluting with water. The yield of crude material was a little over 6 grams. When crystallized from alcohol it formed large, stout, colorless, transparent prisms and melted, to a clear liquid, at 172° – 173° .5.

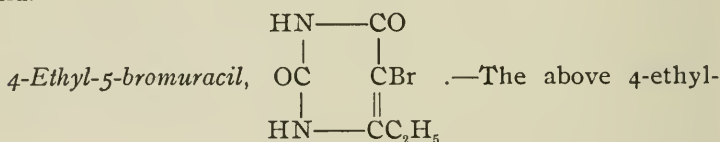
	Calculated for $C_8H_{11}ON_2SBr$.	Found.
N	10.64	10.64



pyrimidine dissolves in concentrated hydrochloric acid but is precipitated again by adding water. It was digested on the steam-bath, with strong hydrochloric acid, for some time and then evaporated to dryness. The residue was more readily soluble in water than in alcohol. When crystallized from the latter it formed beautiful, colorless tables or blocks, which melted at 204° to a clear liquid; it effervesced at about 270° .

	Calculated for $C_6H_8O_2N_2$.	Found.
N	20.0	20.2

The same product was obtained by boiling 2-ethylmercapto-4-ethyl-6-oxypyrimidine, melting at 89° , with hydrochloric acid.

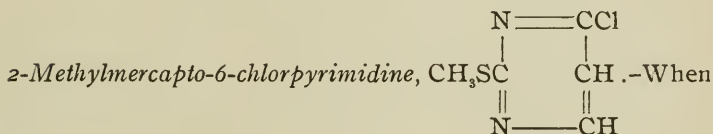


uracil was dissolved in glacial acetic acid, in which it is not very soluble and a slight excess of bromine was added. On cooling, very thin, oblong plates separated. These were difficultly soluble in hot water and crystallized, when slowly cooled, in long, thin, snow-white, glistening prisms that were highly etched. The material crystallized from alcohol in plates, or from strong solution in wisps. At 230° – 231° it melted to a yellow liquid, which immediately turned brown and then effervesced.

	Calculated for $C_6H_7O_2N_2Br$.	Found.
N	12.78	12.62

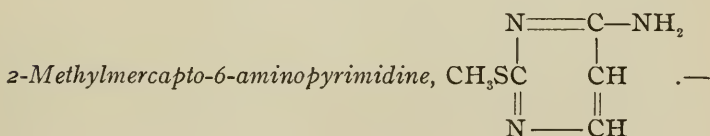
2-Methylmercapto-6-oxypyrimidine Hydrochloride.—This was obtained on passing chlorine into a glacial acetic acid solution of the mercaptopyrimidine and precipitating with ether. It was crystallized from glacial acetic acid and formed prismatic plates, which were washed with ether. It was very soluble in alcohol and water, the aqueous solution giving a strong odor of mercaptan. When boiled with hydrochloric acid, uracil was obtained. It melted, with vigorous effervescence, at 189° .

	Calculated for $C_5H_6ON_2S.HCl$.	Found.
N	15.7	15.8



the above hydrochloride (32 grams) was warmed with the calculated quantity of phosphorus pentachloride and some phosphorus oxychloride, it dissolved and hydrogen chloride was given off. The solution was poured on to ice and extracted with ether, dried and distilled (36 mm.). The colorless oil boiled, for the most part, at 139° – 140° ; on cooling in a freezing mixture it solidified and melted at about -2° – 0° .

	Calculated for $C_5H_5N_2SCl$.	Found.
N	17.4	16.9



The above chloride was heated with a large excess of concentrated alcoholic ammonia, at 120° – 130° , for 3 hours. The ammonium chloride that separated was filtered and the filtrate evaporated to dryness. The residue was treated with water, dried and crystallized from benzene. It formed large, colorless, diamond-shaped, prismatic plates which melted, to a clear oil, at 125° –

126°. It was readily soluble in alcohol and acetone, insoluble in ether and ligroin.

	Calculated for $C_5H_7N_3S$.	Found.
N	29.79	29.76

NEW HAVEN, CONN.,
January, 1905.

Contributions from the Sheffield Laboratory of Yale University.

CXXIII. — RESEARCHES ON PYRIMIDINES: THE ACTION OF POTASSIUM THIOCYANATE UPON SOME IMIDE CHLORIDES.

[NINTH PAPER.]

BY HENRY L. WHEELER AND H. STANLEY BRISTOL.

No attention has hitherto been given to the action of potassium thiocyanate upon imide chlorides. It was, therefore, impossible to predict whether normal thiocyanates, $RSCN$, or isothiocyanates, mustard oils, $RNCS$, would be formed. Most alkyl halides give normal thiocyanates, while the acyl halides give isothiocyanates. Imide chlorides, $-C \begin{smallmatrix} \nearrow N- \\ \searrow Cl \end{smallmatrix}$, are

more closely related to acyl halides, $-C \begin{smallmatrix} \nearrow O \\ \searrow Cl \end{smallmatrix}$, than to the alkyl halides and, in the pyrimidine series, the compounds contain the grouping $C=C-CCl$,¹ therefore isothiocyanates might be expected to be formed in this reaction. This being the case, facilities for further syntheses would be increased.

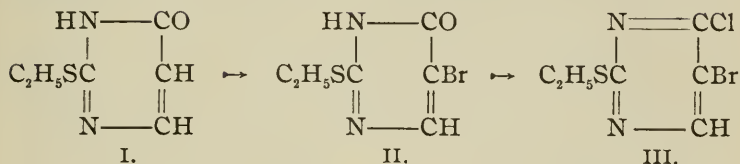
We have investigated this reaction in the case of 2-ethylmercapto-6-chlorpyrimidine, 2-ethylmercapto-5-brom-6-chlorpyrimidine and 2-ethylmercapto-5-methyl-6-chlorpyrimidine and we find, in each instance, that the chlorides give isothiocyanates.

The preparation of derivatives has been more thoroughly carried out in the case of 2-ethylmercapto-5-brom-6-chlorpyrimidine, III., than with the other chlorides. This was prepared, as already shown,² from 2-ethylmercapto-6-oxypyrim-

¹ Compare Wheeler and Jamieson : *J. Am. Chem. Soc.*, **24**, 746 (1902).

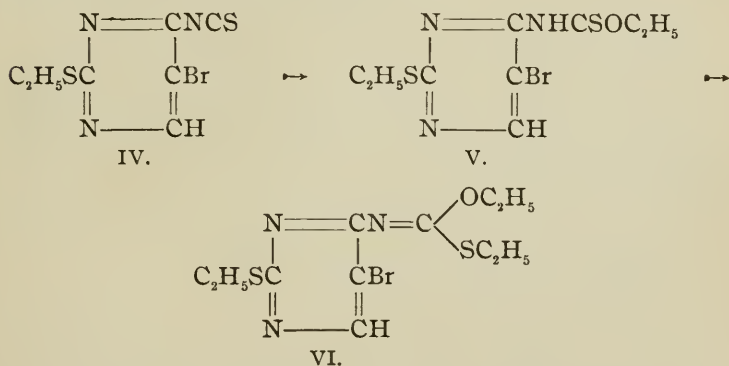
² Wheeler and Johnson : *THIS JOURNAL*, **31**, 603 (1904).

idine (I.) by brominating (II.), then chlorinating in the 6-position.



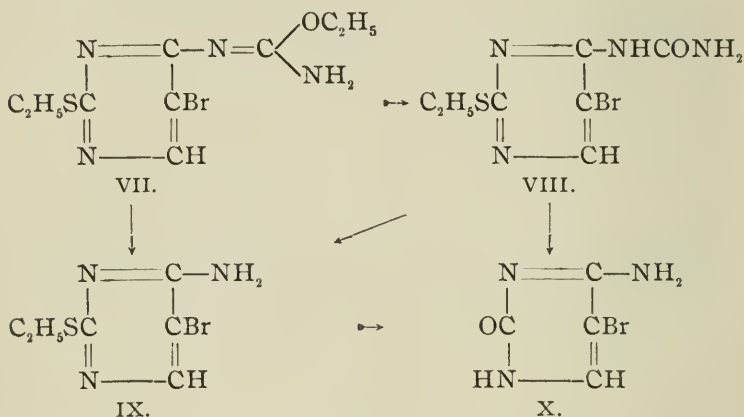
When 2-ethylmercapto-5-brom-6-chlorpyrimidine was boiled, in toluene solution, with potassium thiocyanate, 2-ethylmercapto-5-brom-6-isothiocyanpyrimidine (IV.) was obtained. This reacted with ammonia, aniline, etc., yielding the corresponding thiourea derivatives.

When, however, the chlorbrommercaptopyrimidine (III.) was boiled with an alcoholic solution of potassium thiocyanate, the thionurethane (V.) was obtained and this compound, with sodium ethylate and ethyl bromide, gave the imidothiocarbonic ester represented by Formula VI.



When this imidothiocarbonic ester derivative was treated with alcoholic ammonia, it evolved mercaptan and the pseudo-oxygen urea (VII.) was formed smoothly. This gave the normal urea (VIII.) when treated with cold, concentrated hydrochloric acid. Boiling hydrochloric acid then gave 5-bromcytosine (X.). Attempts to condense the pseudooxygen urea, or the normal urea, to a purin derivative were without success. The bromine in these compounds is firmly bound but the urea and pseudourea groups are easily removed.

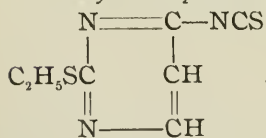
When the pseudourea (VII.) was heated with pyridine or aqueous ammonia, in a closed tube, 2-ethylmercapto-5-brom-6-aminopyrimidine was formed (IX.). The same result was obtained when the compound was boiled with formic acid. Sodium, in boiling benzene, failed to remove bromine but attacked the pseudourea grouping. 2-Ethylmercapto-5-brom-6-aminopyrimidine was also obtained when the normal urea was heated above its melting-point.



In the latter part of this article some new uracil and cytosine derivatives are described.

EXPERIMENTAL.

2-Ethylmercapto-6-isothiocyanpyrimidine,



.—Fifteen grams of 2-ethylmercapto-6-chlorpyrimidine,¹ boiling at 135° (24 mm.) and at 128° (16 mm.) were dissolved in 20 cc. of toluene and 25 grams of dry, powdered potassium thiocyanate were added. The mixture was boiled, in a paraffin-bath, for 12 hours. The insoluble salts were then removed by filtering, the toluene was evaporated and the residue distilled under reduced pressure. It boiled, for the most part, at 180° (32 mm.). The distillate solidified

¹ Wheeler and Johnson: *THIS JOURNAL*, 29, 497 (1903); 31, 596 (1904).

and, when crystallized from benzene, it separated in small, light-yellow, prismatic plates and melted, on slowly heating, at 175°.

	Calculated for $C_7H_7N_3S_2$.	Found.
N	21.32	21.53

2-Ethylmercapto-6-thiourea-pyrimidine,

$$\begin{array}{c}
 \text{N}=\text{C}-\text{NHCSNH}_2 \\
 | \qquad | \\
 \text{C}_2\text{H}_5\text{SC} \quad \text{CH} \\
 || \qquad || \\
 \text{N}-\text{CH}
 \end{array}$$

.—On adding concentrated aqueous

ammonia to a portion of the above toluene solution containing the isothiocyanate, an energetic reaction took place, with evolution of heat and a solid mass separated. When this material was crystallized from alcohol it formed long, thin, colorless prisms and melted at 214°. It was difficultly soluble in water.

	Calculated for $C_7H_{10}N_4S_2$.	Found.
N	26.17	25.83

2-Ethylmercapto-6-phenylthiourea-pyrimidine was prepared by adding aniline to a toluene solution of the pure crystallized isothiocyanate. A solid separated, with evolution of heat and, when crystallized from alcohol, it formed a felted mass of long, colorless needles resembling cotton. It was almost insoluble in hot water and fairly soluble in hot alcohol, it melted at 205°.

	Calculated for $C_{13}H_{14}N_4S_2$.	Found.
N	19.31	19.10

<i>2-Ethylmercapto-6-thionethylurethane-pyrimidine</i> ,		
$ \begin{array}{c} \text{N}=\text{C}-\text{NHCS}.\text{OC}_2\text{H}_5 \\ \qquad \\ \text{C}_2\text{H}_5\text{SC} \quad \text{CH} \\ \qquad \\ \text{N}-\text{CH} \end{array} $		
.—When 5 grams of 2-ethyl-		

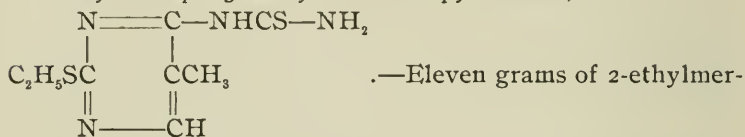
mercapto-6-chlorpyrimidine were added to an alcoholic solution of 2.8 grams of potassium thiocyanate, potassium chloride separated almost at once. The mixture was warmed on the water-bath for 3 hours, the alcohol was then evaporated and the residue treated with water. The crude product weighed 6

grams and, when crystallized from alcohol, it formed long, thin, light-yellow, etched plates, melting at 93° . It is readily soluble in hot alcohol and difficultly soluble in cold.

	Calculated for $C_9H_{13}ON_3S_2$.	Found.
N	17.28	16.89

When this urethane was boiled with concentrated hydrochloric acid, until mercaptan ceased being evolved and then evaporated, a mixture of about equal quantities of uracil and cytosine was obtained.

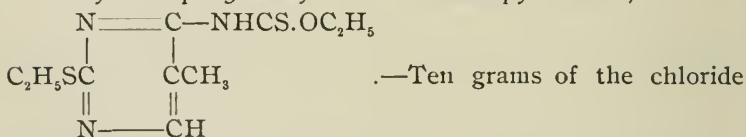
2-Ethylmercapto-5-methyl-6-thioureapyrimidine,



capto-5-methyl-6-chlorpyrimidine, 30 grams of dry, finely powdered potassium thiocyanate and 30 cc. of toluene were mixed and boiled for 7 hours, in an oil-bath. The potassium thiocyanate was added, in portions of 10 grams, from time to time. The mixture was filtered and, to a portion of the solution, alcoholic ammonia was added, the thioureapyrimidine then separated in a fairly pure state. It was moderately soluble in hot alcohol and benzene, difficultly soluble in cold and crystallized from benzene in bunches of radiating needles. It was difficultly soluble in hot water and melted, to a clear oil, at 192° .

	Calculated for $C_8H_{12}N_4S_2$.	Found.
N	24.56	24.30

2-Ethylmercapto-5-methyl-6-thionurethanepyrimidine,



were boiled with 15 grams of dry, finely powdered potassium thiocyanate, in toluene, for 15 hours. Then an excess of alcohol was added and the mixture boiled again for 6 hours. The solution was filtered hot and evaporated to dryness, the residue

treated with water and filtered. It was then taken up in alkali and extracted with ether, the alkaline solution acidified with acetic acid and the pasty, semi-solid precipitate filtered. This was dissolved in ether and dried with potassium carbonate. On evaporation an oil was obtained which solidified completely only after standing 9 months. It was purified by dissolving in benzene and precipitating with ligroin, whereupon groups of pale-yellow prisms separated. It melted at 88° – 89° , to a clear oil. It was readily soluble in alcohol, ether and benzene and difficultly soluble in water.

N	Calculated for $C_{10}H_{15}ON_3S_2$.	Found.
	16.34	16.71

2-Ethylmercapto-5-brom-6-isothiocyanpyrimidine,

$$\begin{array}{c}
 \text{N}=\text{CNCS} \\
 | \qquad \qquad | \\
 \text{C}_2\text{H}_5\text{SC} \qquad \text{CBr} \\
 || \qquad \qquad || \\
 \text{N}=\text{CH}
 \end{array}$$

— The 2-ethylmercapto-5-brom-6-chlor-

pyrimidine, used as the starting-point for the following experiments, was described in a previous paper,¹ but the boiling-point of the material was not given. It was observed to boil at 168° (24–25 mm.) and at 179° – 180° (36 mm.). Fifteen gram portions of the chloride were dissolved in 30 cc. of toluene and 30 grams of finely pulverized, dry potassium thiocyanate were added, in portions of 10 grams each, from time to time. The mixture was boiled for 9 hours, in an oil-bath. It was then filtered and the toluene mostly removed by evaporating on the water-bath, under diminished pressure. Petroleum ether was now added, in slight amount, enough to separate an oily substance. The solutions were quickly poured off from this through a filter and, on standing, beautiful, small, pale-yellow prisms formed, which were purified by dissolving in toluene and adding a small amount of petroleum ether. The material was readily soluble in benzene and toluene and difficultly soluble in petroleum ether. It melted at 79° – 80° .

N	Calculated for $C_7H_6N_3S_2Br$.	Found.
	15.21	15.45

¹ Wheeler and Johnson: THIS JOURNAL, 31, 603 (1904).

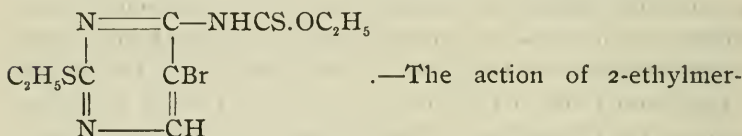
2-Ethylmercapto-5-brom-6-thiourea-pyrimidine.—A portion of the toluene solution of the isothiocyanate was mixed with alcoholic ammonia in excess. Heat was evolved and the thiourea separated at once. It was found to be difficultly soluble in water and alcohol and more soluble in benzene, from which it crystallized in light-yellow plates, melting at 220° .

N	Calculated for	Found.
	$C_7H_9N_4S_2Br$.	
	19.11	18.96

2-Ethylmercapto-5-brom-6-phenylthiourea-pyrimidine.—Aniline acted at once, with evolution of heat, on the isothiocyanate. The product was difficultly soluble in water, fairly soluble in benzene, it separated from alcohol in the form of a felted mass of fine, colorless needles, which melted at 166° – 167° .

N	Calculated for	Found.
	$C_{13}H_{13}N_4S_2Br$.	
	15.17	15.03

2-Ethylmercapto-5-brom-6-thionethylurethane-pyrimidine,



capto-5-brom-6-chlorpyrimidine on potassium thiocyanate, in alcoholic solution, was not smooth. In addition to the thionurethane, two other compounds were isolated as products of the reaction. These were 2-ethylmercapto-5-brom-6-thiopyrimidine and 2-ethylmercapto-5-brom-6-aminopyrimidine.

Thirty-three grams of 2-ethylmercapto-5-brom-6-chlorpyrimidine were added to a concentrated solution of 20 grams of potassium thiocyanate in alcohol and the mixture was boiled for several hours. At the end of this operation the odor of ethylthiocyanate was noticed. The solution was filtered and the alcohol evaporated. The residue was treated with cold benzene and filtered, leaving 2-ethylmercapto-5-brom-6-thiopyrimidine and potassium thiocyanate undissolved. The benzene was then evaporated and the residue treated with dilute sodium hydroxide and extracted with ether. The ether solution con-

tained the 2-ethylmercapto-5-brom-6-aminopyrimidine, melting at 124°, which was described in a previous paper.¹

The urethane was precipitated from the alkaline solution by means of acetic acid; the yield of crude material was 25 grams. It was readily soluble in hot alcohol, difficultly soluble in cold and formed long, pointed, light-yellow, prismatic plates, melting at 82°.

In two other experiments 18.5 grams of the chloride gave 13 grams of the urethane and 15 grams of the chloride gave 11.5 grams of the urethane.

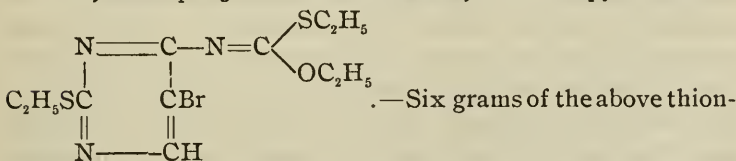
	Calculated for C ₉ H ₁₂ ON ₂ S ₂ Br.	Found.
N	13.04	12.97
$ \begin{array}{c} \text{HN} \text{---} \text{CS} \\ \qquad \\ \text{C}_2\text{H}_5\text{SC} \quad \text{CBr.} \\ \qquad \\ \text{N} \text{---} \text{CH} \end{array} $		

—The residue, left undissolved by cold benzene, in the above preparation was washed with water, dried and crystallized from benzene. It formed pointed, etched, pale-yellow plates and melted, with slight effervescence, at 198°.

	Calculated for C ₆ H ₇ N ₂ S ₂ Br.	Found.
N	11.15	11.04

In the course of some other work Mr. S. H. Clapp prepared this compound, by the action of potassium hydrosulphide on 2-ethylmercapto-5-brom-6-chlorpyrimidine. When this preparation was mixed with the above the melting-point was not altered.

2-Ethylmercapto-5-brom-6-iminothioethylcarbonatepyrimidine,



ethylurethane were dissolved in a solution of 0.42 gram of sodium, in a small quantity of absolute alcohol and then 4 grams

¹ THIS JOURNAL, 31, 604 (1904).

of ethyl bromide were added. On standing a short time sodium bromide separated. The mixture was warmed on the steam-bath, then filtered and evaporated to dryness. The product was treated with ether, filtered from sodium bromide and evaporated. The residue, on cooling, solidified. The yield was found to be 6 grams. The product was purified by crystallizing from alcohol containing a little water. It then formed long, colorless prisms, melting at 43° , which were readily soluble in alcohol, ether and warm ligroin but insoluble in water.

N	Calculated for $C_{11}H_{16}ON_2S_2Br$.	Found.
	12.00	11.87

2-Ethylmercapto-5-brom-6-pseudoethylureaprimidine,

$$\begin{array}{c}
 N=C-N=C-OC_2H_5 \\
 | \quad \quad | \quad \quad | \\
 C_2H_5SC \quad CBr \quad NH_2 \\
 || \quad \quad || \\
 N-CH
 \end{array}$$

—This was formed, quantita-

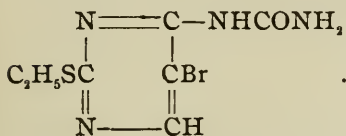
tively, by passing ammonia gas into an alcoholic solution of the above aminothioethylcarbonate. It crystallized from alcohol in beautiful, long needles, which developed into thin plates, melting at 110° and decomposing about 230° , forming a tarry mass on cooling. It was difficultly soluble in hot water and insoluble in cold, dissolved readily in cold benzene and warm alcohol. It was insoluble in alkali and soluble in hydrochloric acid.

N	Calculated for $C_9H_{13}ON_4SBr$.	Found.
	18.3	18.1

This material can be boiled with pyridine (3 hours) or dimethyl aniline (10 minutes) and recovered unaltered. No bromine is removed under these conditions. When heated with pyridine at 180° – 190° , in a closed tube, for 5 hours, the only crystalline substance obtained was 2-ethylmercapto-5-brom-6-aminopyrimidine. This substance was also obtained when the material was boiled with formic acid. A nitrogen determination gave 17.7 per cent, while the calculated is 17.9 per cent. The action of concentrated aqueous ammonia, in a closed tube, first at 90° for 3 hours, then at 145° – 150° for 4½

hours, gave the same result. The hydrochloride of this base was obtained when the pseudourea was warmed, for a short time, with concentrated hydrochloric acid. About 0.5 gram of the pseudourea was dissolved in benzene and treated with an excess of sodium, the mixture was boiled for 12 hours. The metal became coated with a thick deposit and, on filtering and evaporating the benzene, there was no residue. The sodium and coating was treated with alcohol and a portion was acidified with nitric acid, whereupon silver nitrate gave no insoluble precipitate, and, therefore, no bromine had been removed. On acidifying the alkaline solution with acetic acid and evaporating, a substance was obtained melting at 287° , with effervescence. On dissolving in acetone and precipitating with ether it effervesced at 310° . It was concluded that this material was *2-ethylmercapto-5-brom-6-cyanamidepyrimidine*, not only from its mode of formation, but also because, on warming with dilute hydrochloric acid, it gave the following urea derivative :

*2-Ethylmercapto-5-brom-6-urea*pyrimidine,



.—This was also produced by al-

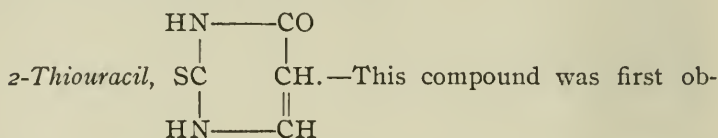
lowing the above pseudourea to stand dissolved in cold concentrated hydrochloric acid. After several days the urea separated on adding water. It crystallized from alcohol in short, pointed plates which, on long standing, developed into stout prisms and melted, when slowly heated, at 167° .

	Calculated for $\text{C}_7\text{H}_9\text{ON}_4\text{SBr}$.	Found.
N	20.2	19.8

If this material is heated to its melting-point, cooled and reheated, it melts unaltered. If the heating is continued a little above its melting-point it slowly becomes semi-solid. One gram of the urea derivative was heated, in a test-tube, at 170° – 180° , a portion sublimed, crystallizing in prismatic plates in the cool part of the tube. This melted at 124° and, when

mixed with some 2-ethylmercapto-5-brom-6-aminopyrimidine, the melting-point was not altered.

When this urea was boiled with concentrated hydrochloric acid 5-bromcytosine¹ was obtained.



tained, along with 2-ethylmercapto-6-oxypyrimidine, when pseudoethylthiourea, containing some thiourea, was condensed with ethyl sodium formylacetate. A concentrated aqueous solution of 150 grams of ethyl sodium formylacetate was mixed with a saturated solution of 50 grams of thiourea. The mixture was then warmed on the steam-bath for a short time, cooled and the deep red solution was precipitated with a slight excess of acetic acid. A yellowish-white, granular precipitate separated, weighing 50 grams. This crystallized from alcohol or water in colorless prisms. It is difficultly soluble in these solvents. When heated, it effervesces above 300°.

	Calculated for C ₄ H ₄ ON ₂ S.	Found.
N	21.8	21.9

2-Ethylmercapto-6-anilinopyrimidine hydrochloride was prepared by mixing 2-ethylmercapto-6-chlorpyrimidine (10 grams) with aniline (5.3 grams), after standing over night, then warming on the water-bath for several hours, the mixture solidified. It was readily soluble in hot alcohol and hot water and crystallized in the form of colorless needles or prisms. It melted at 198° with effervescence.

	Calculated for C ₁₂ H ₁₄ N ₃ SCl.	Found.
N	15.7	15.9

When this hydrochloride was dissolved in hot water and precipitated with ammonia, an oil separated. This finally solidified and was purified by repeatedly dissolving in alcohol and precipitating with water. The base is very soluble in alcohol. It formed fine, colorless needles and melted at 68°.

¹ THIS JOURNAL, 31, 604 (1904).

	Calculated for $C_{12}H_{13}N_3S$.	Found.
N	18.1	18.2

$2\text{-Oxy-6-anilinopyrimidine (Phenylcytosine),}$

$$\begin{array}{c} \text{N} \\ \text{N}=\text{C}-\text{NHC}_6\text{H}_5 \\ | \quad | \\ \text{OC} \quad \text{CH} \\ | \quad || \\ \text{HN}-\text{CH} \end{array}$$

—The hydrochloride of this base was

obtained by boiling the above hydrochloride with strong hydrochloric acid. It formed colorless needles or prisms, from water or alcohol, which effervesced at 228° . This material was dissolved in hot water and ammonia was added, whereupon bunches of colorless needles separated. Unlike cytosine, this substance crystallizes without water of crystallization. It is fairly soluble in hot alcohol and, from this solvent, it separates in beautiful, colorless, six-sided plates. When slowly heated it melted at about 269° .

	Calculated for $C_{10}H_{10}ON_3$.	Found.
N	22.3	22.6

The *chlorplatinate* formed groups of radiating yellow prisms. A platinum and water determination agreed with the calculated for a normal salt with 1 molecule of water of crystallization. The formation of platinum chloride double salts with water of crystallization seems to be of frequent occurrence in the pyrimidine series.

	Calculated for $(C_{10}H_{10}ON_3)_2H_2PtCl_6 \cdot H_2O$.	Found.
Pt	24.24	24.31
H_2O	0.22	0.26

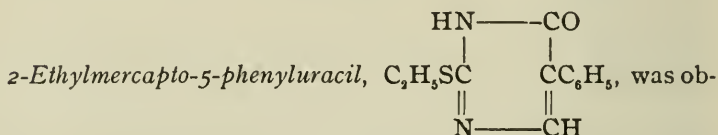
	$\begin{array}{c} \text{N} \\ \text{N}=\text{C}-\text{NHC}_6\text{H}_5 \\ \quad \\ \text{C}_6\text{H}_5\text{NHC} \quad \text{CH} \\ \quad \\ \text{N}-\text{CH} \end{array}$	
$2,6\text{-Dianilinopyrimidine,}$		—The

hydrochloride of this base was obtained when 2-ethylmercapto-6-chlorpyrimidine was heated to 150° , with 2 molecular proportions of aniline. The compound formed arborescent needles from alcohol and melted at 197° .

	Calculated for $C_{16}H_{15}N_4Cl$.	Found.
N	18.76	18.59

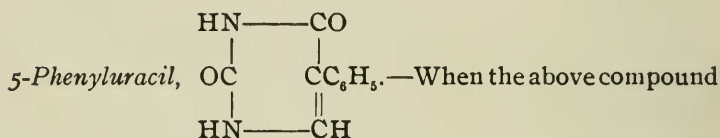
The free base, obtained by boiling the hydrochloride with aqueous ammonia, crystallized from alcohol in six-sided plates. It is insoluble in water and fairly soluble in hot benzene and ether. It melted at 136° – 137° .

N	Calculated for	Found.
	$C_{16}H_{14}N_4$.	
	21.38	21.42



tained by condensing sodium phenylformylethylacetate¹ with the ethyl iodide addition-product of thiourea, in alkaline solution. The yield was very poor. The substance crystallized from alcohol in long, needle-like prisms, melting at 158° . In alcohol and hot water it is readily soluble.

N	Calculated for	Found.
	$C_{12}H_{12}ON_2S$.	
	12.07	12.12



was digested on the steam-bath, with concentrated hydrochloric acid, for a number of hours, mercaptan was evolved and difficultly soluble material was obtained. The product was sparingly soluble in hot alcohol and water, but it separated from these solutions, on cooling, in a flocculent mass of what appeared to be microscopic plates. It did not melt at 350° . It is soluble in alkali and can be precipitated unaltered by hydrochloric acid.

N	Calculated for	Found.
	$C_{10}H_8O_2N_2$.	
	14.89	14.87

The isomeric 4-phenyluracil has been described by Fischer and Roeder² and it was also obtained by one of us.³

NEW HAVEN, CONN.,
January, 1905.

¹ Wislicenus: Ber. d. chem. Ges., 20, 2933 (1887).

² *Ibid.*, 34, 3751 (1901).

³ Wheeler and Merriam: THIS JOURNAL, 29, 490 (1903).

X.—CASEIN AND PARACASEIN IN SOME OF THEIR RELATIONS TO BASES AND ACIDS.

BY LUCIUS L. VAN SLYKE AND EDWIN B. HART.

For several years we have been studying the chemical changes that occur in the process of cheese-making and cheese-ripening. Early in our work we extracted fresh and partially ripened cheese with dilute solution of sodium chloride, following a suggestion of Chittenden,¹ who had shown that, in a peptic digestion of casein, heterocaseose was formed only in small amounts.

As we obtained, by our extraction with dilute salt solution, amounts of proteid representing often as much as 75–80 per cent of the total nitrogen present in the cheese, it became apparent that we were dealing with some compound other than heterocaseose. The first suggestion, throwing any light on the method of formation of this salt-soluble substance, came in the following manner: In studying the action of galactase in cheese-ripening, we made cheddar cheese from milk containing chloroform, added for the purpose of inhibiting bacterial action. Under these conditions no lactic acid was present. In order to approximate more closely to the conditions present in normal cheddar cheese we added, in a parallel experiment, a small quantity of lactic acid, the other conditions being kept uniform. We noticed at once that, when no acid was present in the cheese, we found little or no salt-soluble substance, while in the cheese containing a little added lactic acid there were present marked quantities of the salt-soluble product. This fact suggested that lactic acid was a necessary agent in forming the salt-soluble proteid found by us in cheese. Hence we were led to believe that there is a chemical combination between the paracasein of the fresh cheese-curd and the lactic acid formed from milk-sugar during the cheese-making process. We were also able to form salt-soluble proteids by treating paracasein with such acids as acetic, hydrochloric and sulphuric. In each case definite amounts of acid disappeared

¹ "Studies in Physiol. Chem.," Yale Univ., 2, 156 (1885–6).

and the proteid treated underwent marked and definite changes in properties. By treating the salt-soluble compound with about the same amount of acid as was required to form it from paracasein, we obtained a body insoluble in salt solution and differing also in other properties. We were thus led to conclude that two series of salts were formed by treating paracasein with acids, one containing twice as much acid in combination as the other. We therefore called the salt-soluble compound, found in normal cheddar cheese, paracasein monolactate and the one insoluble in salt solution, paracasein dilactate. We also found the same behavior in the case of milk-casein when treated by acids. The two series of compounds varied in respect to many of their properties.¹ Our conclusions were based upon the fact that, when casein or paracasein is treated with an acid in definite quantities, we obtain compounds of definitely characteristic properties.

We desired, however, if possible, to carry our work farther and prove, beyond question, that there is an actual chemical combination between acid and proteid. We wished to prepare the free proteid and then treat this with acid and study the results.

Hammarsten² made a special study of the interaction of casein and acids and concluded that there was no ground for believing that a chemical combination takes place between casein and the acid used to precipitate it. He based his statement on the fact that, by triturating for several days, in a mortar, with different portions of water, a precipitate formed by casein with an acid, he was able to remove the acid so completely that the remaining precipitate gave no test for it. The substance which he used in his work was what we have called a di-acid compound of casein. In repeating Hammarsten's work we were able to obtain a substance free from the acids used as precipitants and also practically free from ash. We found this substance, when freshly prepared, readily soluble in warm dilute salt solution and in hot dilute alcohol; it also showed the ductile and plastic properties of the substance we called a mono-salt of casein. The facts, as they presented

¹ THIS JOURNAL, 28, 411-438 (1902).

² Maly: *Jahres. d. Thierchemie*, 7, 160 (1877).

themselves to us at this point, were as follows: A precipitate, formed by treating milk-casein with an acid, being what we called a di-salt of casein, was, by continuous washing and trituration, converted into a substance free from the acid used as precipitant and nearly free from ash; the substance precipitated by acid, insoluble in warm dilute salt solution and in hot 50 per cent alcohol, was, by continuous trituration under water and washing, converted into a substance easily soluble in warm dilute salt solution and in hot 50 per cent alcohol. There was also a simultaneous change in other properties. Thus, what we called a di-salt of casein was changed into what we had termed a mono-salt of casein, but the latter was free from acid and ash.

In our early study we recognized, in a limited way, the relation of inorganic salts in milk to the neutralization of acid. We noticed that when milk, coagulated by rennet enzyme, is treated with varying amounts of acid, the quantity of salt-soluble substance did not increase until a certain amount of acid had been added, after which it increased quite out of proportion to the larger amount of acid used. It was suggested that the formation of the salt-soluble compound did not begin until certain inorganic salts of the milk had been neutralized.¹

After developing the later facts described above, we decided to study more fully the following questions:

1. What is the relation between milk-casein and the salt-soluble compounds which we have called casein mono-salts?
2. What is the relation between the two series of compounds previously called casein mono-salts and casein di-salts?
3. What is the relation of casein and its derivatives to paracasein and its derivatives?

It may be well to state, once for all, that our work deals exclusively with the casein of cows' milk and the products derived from it.

The Relation of Milk-Casein to the Casein Compounds Soluble in Dilute Salt Solutions.

A study of the relation of milk-casein to the salt-soluble substance, which we have previously called a casein mono-salt,

¹ THIS JOURNAL, 28, 428 (1902).

naturally resolves itself into a study of the two following questions: (1) What is milk-casein, especially in relation to inorganic compounds? (2) What is the salt-soluble compound formed from milk-casein?

The Relation of Inorganic Compounds to Milk-Casein.—Does casein, as it is found in cows' milk, exist as a free proteid, or is it in some form of combination with an inorganic compound?

Hammarsten, who must be regarded as the most successful pioneer worker in this field, has not clearly and specifically stated what he considers milk-casein to be. He does not appear to make any chemical distinction between ash-free casein, as prepared from cows' milk by his well-known method and casein as it is found in milk. He appears to favor the idea that there is, in milk-casein, some kind of physical relation between the proteid and calcium phosphate, casein acting as a solvent for calcium phosphate.¹ Eugling² held that casein enters into combination with tricalcium phosphate and the same view was held by Schaeffer.³ Söldner⁴ showed that casein, prepared from cows' milk, can form two calcium salts, (1) a basic calcium casein, containing about 2.36 per cent of calcium oxide, neutral to phenolphthalein, but alkaline to litmus; (2) a neutral calcium casein, containing about 1.55 per cent of calcium oxide, slightly acid to phenolphthalein and neutral or slightly alkaline to litmus. Söldner believed that this neutral calcium casein is probably the form existing in milk, owing to its reaction and to its coagulability by rennet in the presence of soluble calcium salts. He also held that calcium phosphate, usually found in casein precipitates, exists in a condition of suspended particles, finely divided and not in chemical combination with casein. Courant⁵ confirmed the work of Söldner, calling the basic calcium compound tri-calcium casein and the neutral compound di-calcium casein. He also reported, on what seems to us as rather intangible evidence, a mono-calcium casein, the existence of which has not been confirmed and appears doubtful. He regards milk-casein as made up partly of

¹ Maly: *Jahres. d. Thierchemie*, **4**, 146 (1874).

² *Landw. Versuchs-Stat.*, **31**, 392 (1885).

³ *Landw. Jahrb. d. Schweiz*, **1**, 33 (1887).

⁴ *Landw. Versuch-Stat.*, **35**, 351 (1888).

⁵ *Pflügers Arch.*, **50**, 109 (1891).

di- and partly of mono-calcium casein. Courant's work was entirely volumetric and no attempt was made to isolate the individual compounds. Lehman and Hempel¹ regard milk-casein as a double compound, formed by the combination of calcium casein and calcium phosphate.

Our work confirms Söldner's, which was carried on mostly by volumetric methods, whereas we have succeeded in isolating the two calcium casein compounds described by him.

Preparation of Casein.—We prepared caesin by Hammarsten's method, repeating the precipitation and solution 4 times. The precipitate was finally dissolved in 20 liters of very dilute ammonia water and precipitated by dilute acetic acid. The precipitate was ground in a mortar several times, with water, then with alcohol, after which it was treated with ether and dried at 100°. Thus prepared, the casein contained only 0.042 per cent of ash. The preparation was still slightly soluble in warm salt solution and in hot 50 per cent alcohol.

Behavior of Casein Preparation toward Calcium Carbonate.—We rubbed in a mortar 0.5 gram of the casein preparation described above with finely divided calcium carbonate, suspended in water. The mixture was filtered several times through paper, giving a slightly opalescent solution. This solution was precipitated by 95 per cent alcohol, the precipitate was washed several times with alcohol, then treated with ether and dried at 100°. The product contained 2.46 per cent of calcium oxide, agreeing very closely with Söldner's work, in which he showed, by an indirect method, that a casein preparation, treated with calcium carbonate, combined with 2.39 per cent of calcium oxide. A part of this calcium casein preparation was dissolved in dilute ammonia, reprecipitated by dilute acetic acid and the precipitate, after thorough washing and filtering, was again obtained practically ash-free.

Solubility of Casein Preparation in Lime-Water.—We dissolved 3 grams of our original casein preparation in lime-water and obtained an opalescent solution.

Preparation of Basic Calcium Casein.—The lime-water solution of casein was made neutral to phenolphthalein by N/10

¹ Pflügers Arch., 56, 558 (1894),

hydrochloric acid and became somewhat more milky. This solution was treated with 95 per cent alcohol and the resulting precipitate, which readily separated, was washed several times with alcohol, finally with ether and dried at 100° . This precipitate contained 0.75–1.2 per cent of calcium chloride, either as the result of occlusion or, possibly, of a loose combination with the proteid. Chlorine and calcium determinations were made with the following results: 1.24 grams of material yielded 0.0331 gram of CaO. There was present 0.0063 gram of Cl, equivalent to 0.0097 gram of CaCl_2 , or 0.0047 gram of CaO. This would leave 0.0284 gram of CaO combined with casein, or 2.29 per cent. The compound was, therefore, the basic calcium casein of Söldner. It was insoluble in 5 per cent salt solution and in hot 50 per cent alcohol.

Preparation of Neutral Calcium Casein.—When a solution of casein in lime-water is made neutral to phenolphthalein, the basic calcium casein is formed containing about 2.40 (2.29–2.46) per cent of calcium oxide. When the addition of acid is carried farther, a point is reached where the solution becomes neutral to litmus and much more milky in appearance than the solution neutral to phenolphthalein. A solution of casein in lime-water was made neutral to litmus by the addition of N/10 hydrochloric acid; to this solution alcohol was added, throwing down a white precipitate. The precipitate was washed with alcohol and ether and dried at 100° . It contained 1.13 per cent of calcium chloride. Analysis: 1.27 grams gave 0.0257 gram of CaO and 0.0093 gram of Cl, equivalent to 0.0072 gram of CaO, leaving 0.0185 gram of CaO or 1.46 per cent as combined with the proteid. Söldner recognized this combination and attributed to it a content of 1.55 per cent of calcium oxide. Another preparation contained 0.86 per cent of calcium chloride and 1.48 per cent of calcium oxide combined with casein.

Behavior of Calcium Casein Solution toward Rennet Enzyme and Calcium Chloride.—A solution of basic calcium casein, the compound neutral to phenolphthalein, is not coagulated by rennet enzyme either in the presence or absence of soluble calcium salts, such as calcium chloride. A solution of neutral calcium

casein, the compound neutral to litmus, is coagulated by rennet in the presence of soluble calcium salts. When soluble calcium salts are removed by ammonium oxalate, no coagulation occurs. These statements are in agreement with the observations of others.

Casein Present in Milk as Neutral Calcium Casein.—Our results appear to confirm, in every respect, the work of Söldner in regard to the relation of inorganic compounds to milk-casein. We have had the advantage of isolating the two compounds, which with him were more largely matters of inference. Of these two calcium casein derivatives, the one containing about 1.55 per cent of calcium oxide, neutral to litmus and coagulable by rennet enzyme in the presence of soluble calcium salts, appears to meet all the requirements of milk-casein.

The Behavior of Calcium Casein Compounds toward Soluble Calcium Salts.—Basic calcium casein, prepared by dissolving free casein in lime-water and making neutral to phenolphthalein by acid, is coagulated by soluble calcium salts on warming at 35°–40°. The coagulum is insoluble in warm, 5 per cent salt solution. If any soluble calcium salts present are removed by treatment with ammonium oxalate, the basic calcium casein is not coagulated on warming.

Neutral calcium casein, prepared by dissolving free casein in lime-water and making neutral to litmus, is coagulated on warming by soluble calcium salts. The coagulum is insoluble in warm dilute salt solution. The neutral calcium casein existing in milk is coagulated, on warming, by a few drops of calcium chloride solution. If we add to milk an amount of acid insufficient to cause coagulation, or to remove from its combination the calcium of the calcium casein, we can produce some coagulation on warming. This is probably due to the conversion of insoluble into soluble calcium salts and the same result follows as when we add a soluble calcium salt directly to the milk.

The coagulation of calcium casein compounds, by a soluble calcium salt, may be due to purely physical change in the calcium casein compounds, or there may be a loose chemical com-

bination between the soluble calcium salt and the calcium casein derivatives, the resulting compound being insoluble in the neutral or slightly acid medium.

The Relation of the Salt-Soluble Compound of Casein to Milk-Casein.—The preparations of calcium casein, while slightly soluble in hot 50 per cent alcohol, were insoluble in warm 5 per cent salt solution. None of them showed, in any marked degree, the properties of the compounds that we have called casein mono-salts. We have already called attention to the fact that, in making an ash-free preparation of casein from cows' milk, we found it to be readily soluble in both warm dilute salt solution and in hot 50 per cent alcohol. This suggested that there might be a close relation between these compounds and we therefore made several preparations, the details of which we now give.

Preparation 1, by the Use of Hydrochloric Acid.—Two liters of skimmed milk were diluted with 5 volumes of distilled water and the mixture was warmed to 45°. Dilute hydrochloric acid was added, accompanied by vigorous stirring to keep the precipitate in a finely divided condition. After the precipitate had settled, the supernatant liquid was poured off, the precipitate was triturated in a mortar with water and finally allowed to drain on filter-paper. It was then removed from the filter-paper, mixed with water at 45°–50°, triturated and filtered again. This was repeated 4 or 5 times a day and continued until the filtrate gave no test for chlorides, which required 4 days. When the precipitate had finally been drained it was washed with 95 per cent alcohol. Some of the proteid went into solution, owing to dilution of the alcohol by the water still present in the precipitate and this partial solution stopped only after a large volume of alcohol had been used. The precipitate was finally washed with ether and dried at 100°. The product was a very friable, white powder. It was still somewhat soluble in hot 50 per cent alcohol and warm 5 per cent salt solution. These solubilities are much more marked before treatment with strong alcohol and ether. The product was practically ash-free, 5.28 grams yielding 0.02 per cent of ash. The preparation was quite free from chlorides, this being

shown in the following manner: We dissolved 0.5 gram in hot, concentrated nitric acid, to which was added a crystal of silver nitrate. The whole was boiled until complete solution of the proteid had occurred. No precipitate of silver chloride was formed.

Preparation 2, by Hammarsten's Method.—We used 2 liters of skim-milk and followed in exact detail the method described by Hammarsten.¹ Before treatment with alcohol this preparation was readily soluble in warm dilute salt solution and in hot 50 per cent alcohol. It contained 1.06 per cent of ash. It was shown to be free from acetate in the following manner: We dissolved 0.5 gram in dilute sodium hydroxide, then precipitated the proteid by hydrochloric acid and filtered. The filtrate was made alkaline and evaporated to dryness. The residue gave no evidence of ethyl acetate when heated with alcohol and sulphuric acid.

Preparation 3, by the Use of Hydrochloric Acid.—We used 2 liters of skim-milk, diluting it with 15 liters of distilled water and precipitating the casein by hydrochloric acid. The separated proteid was allowed to drain on filter-paper and washed with water at 45°. It was then mixed with water and triturated and washed several times. The precipitate soon showed marked solubility in warm dilute salt solution and hot 50 per cent alcohol. The washing was continued until all chlorides were removed. The precipitate was finally washed with alcohol and ether and dried at 100°. It was free from chlorides. Its solubility in alcohol or salt solution was now slight. The ash content was 0.81 per cent. We have noticed that the degree of fineness of the proteid, after precipitation, largely influences the ash content.

Preparation 4, by the Use of Sulphuric Acid.—The same method was followed as that described in preparation 3, except that we used sulphuric acid as the precipitant in place of hydrochloric acid. Triturating this preparation, under different portions of water, 4 or 5 times a day, we had to continue the operation 19 days before the filtrate failed to show the presence of sulphuric acid. A little chloroform was added from time to

¹ Maly: Jahres. d. Thierchemie, 7, 159 (1877).

time, to prevent bacterial action. The proteid was found to be entirely free from sulphuric acid. The extreme difficulty in removing the sulphuric acid was due to the formation of calcium sulphate in the first precipitation and to its slow solubility in water. This preparation had an ash content of 0.56 per cent. During the process of removing the sulphuric acid the precipitate was readily soluble in hot 50 per cent alcohol and in warm 5 per cent solution of sodium chloride. After treatment with alcohol these solubilities were almost entirely lost.

Preparation 5, made from Lime-Water Solution of Casein.—If we dissolve an ash-free preparation of casein in lime-water and add N/10 hydrochloric acid until blue litmus is just turned red, no visible separation of proteid occurs. If we continue to add acid the proteid separates and complete precipitation occurs when all the calcium in the original lime-water solution has been neutralized. This can be shown quantitatively in the following manner: Of the lime-water employed, 50 cc. required for neutralization 19.2 cc. of N/10 hydrochloric acid, using phenolphthalein. We dissolved 0.5 gram of ash-free casein in 50 cc. of this lime-water. On titration, the neutral point, with phenolphthalein, was reached when we had used 15.2 cc. of N/10 hydrochloric acid. This means that calcium oxide, equivalent to 4 cc. of N/10 hydrochloric acid, was no longer present as calcium hydroxide, that is, 0.0112 gram of calcium oxide. This amount had combined with the 0.5 gram of proteid, forming 2.24 per cent of the calcium proteid compound and this proportion indicates the basic calcium casein.

When we had added 16.4 cc. of N/10 hydrochloric acid the solution was just blue to litmus. This indicates that calcium oxide, equivalent to 2.8 cc. of N/10 hydrochloric acid, or 0.00784 gram of calcium oxide, was no longer present as calcium hydroxide but had combined with the 0.5 gram of proteid, forming 1.57 per cent of the calcium proteid combination; this proportion indicates the neutral calcium casein.

When we had added 16.6 cc. of N/10 hydrochloric acid to the lime-water solution of casein, litmus was turned red, but no precipitation occurred. After 18.5 cc. of N/10 hydrochloric

acid had been added a precipitate began to form and was complete when we had added 19.2 cc. N/10 hydrochloric acid, or just enough to combine with all the calcium originally present in the solution used. This work was repeated with closely agreeing results. *This precipitate is, therefore, base-free casein.* A preparation, made in this manner and thoroughly washed, showed that all the calcium was present as calcium chloride, either occluded in the precipitate or, possibly, in a loose form of combination with the proteid; in any case there was no calcium oxide in combination with the casein. The precipitate contained, in 1 gram, 0.00343 gram of calcium and 0.0064 gram of chlorine, which amounts agree well for the presence of calcium chloride. This body, prepared by neutralizing a solution of calcium casein, is insoluble in water but readily soluble in 5 per cent solution of sodium chloride and in hot 50 per cent alcohol.

In another experiment, 25 cc. of lime-water required 10.6 cc. of N/10 hydrochloric acid to neutralize it. We dissolved, in this amount of lime-water, 0.5 gram of ash-free casein, prepared according to Hammarsten. To precipitate this quantity of casein completely required 10.6 cc. of N/10 hydrochloric acid. The precipitated substance was soluble in warm dilute salt solution and in hot dilute alcohol. To the compound we added 0.5 cc. of N/10 hydrochloric acid and obtained a substance insoluble in warm dilute salt solution and only slightly soluble in hot dilute alcohol.

When the product, made by neutralizing the lime-water solutions of ash-free casein with hydrochloric acid, was dissolved in hot 50 per cent alcohol, the dissolved proteid separated from the solution on cooling, forming, on the bottom of the beaker, a gummy, sticky mass, which could easily be gathered on the end of a glass rod. When the substance, freshly precipitated from its solution in lime-water, is warmed on the water-bath it can also be easily gathered on a glass rod in an adherent, gummy mass. When warm, it is plastic and can be drawn out in long, fine, silky threads.

Identity of Base-Free Casein and the Salt-Soluble Body.—In the presentation of the preceding facts we have seen that, when an

ash-free, *i. e.*, base-free proteid, or one practically so, is prepared by precipitating milk-casein (calcium casein) with an acid, the acid precipitant being completely removed from the proteid by long-continued trituration in water; or when a base-free proteid is prepared by treating a lime water solution of a base-free casein with an acid just to the point of acidity with litmus, we obtain a body which is soluble in warm 5 per cent salt solution and in hot 50 per cent alcohol. This substance, when freshly prepared and warmed, is very plastic and is capable of being drawn into very long, fine, silky threads. It behaves in all respects like the compound which we were led to regard, at first, as formed by combination of casein and an acid and which we regarded as a casein mono-salt of the acid precipitant. As a result of this work, we now believe that the compound formed by treating milk with an amount of acid just sufficient to combine with the calcium of the calcium casein, in addition to certain inorganic salts of the milk, is not a casein mono-salt of the acid precipitant but *is base-free casein or calcium casein (milk-casein) from which the calcium has been removed by combination with acid.*

The Relation between the Two Series of Compounds Previously Called Casein Mono-salts and Casein Di-salts.

We have already seen that, when calcium casein (milk-casein) is treated with dilute acid, the base is removed from its combination with the proteid and the base-free proteid is formed, a compound corresponding in its properties to those of the compounds we formerly called casein mono-salts of acids. When, to this base-free proteid, we add a dilute acid, another body appears to be formed, which is insoluble in warm 5 per cent salt solution and in hot 50 per cent alcohol and which differs also in a marked lack of the plastic properties exhibited by the base-free proteid when freshly prepared and warmed. It is the familiar substance ultimately formed when milk is coagulated by ordinary souring, or by direct addition of acids in sufficient quantity. The formation of this substance has usually been explained in two different ways:

(I.) It has been quite generally held that the acid unites with the inorganic portion (calcium) of the milk-casein, thus

destroying the combination the free proteid then appearing as a solid.

(II.) It has been supposed by some that the acid actually combines with the proteid, forming a casein salt of the acid used. According to the first explanation, only one substance is formed when milk-casein is precipitated with an acid and that is the base-free casein. According to the second explanation, two compounds are formed, one after the other, by treating milk-casein with an acid, *viz.*, (1) the base-free casein ; (2) a compound formed by the combination of the base-free casein with the acid.

The existence must be acknowledged of one body with two different sets of properties, or of two different bodies, differing in their properties, when we treat milk-casein with an acid in proper proportions, because, by treating calcium casein with a certain amount of acid, we obtain the base-free proteid and then, by treating this with an additional amount of acid, a body differing in properties from the base-free proteid is formed ; the difference must either be due to chemical combination of the proteid and acid or else be the result of a purely physical change caused by the acid. Contrary to the view generally held, we have believed that there was actual combination between the proteid and acid, forming a casein salt of the acid and this we formerly called a casein di-salt of the acid used. Since we have shown that our supposed casein mono-salts of acids are simply the base-free casein, it would appear that there is only one series of casein compounds formed by combination with acids, existing as a precipitate.

Hammarsten held that there could be no combination between the casein and acid, because, by trituration with water in a mortar, he was able to remove the acid completely from the proteid. We have abundantly confirmed his statement that the acid can be removed from the proteid by long-continued trituration, but, in view of recent developments in chemistry, this argument has no weight, because we can do the same thing in the case of some well-known and well-established inorganic salts. For example, the sulphuric acid radical of mercuric sulphate can be readily and completely removed by triturating with water.

Experiments Showing Combination of Casein and Acids.—In order to show that there is actual combination between base-free casein and acids, we used the following method: We suspended, in 50 cc. of distilled water, 0.5 gram of finely-ground base-free casein and allowed the mixture to stand 1 hour, with occasional shaking. At the end of this time we added hydrochloric acid, of known strength, in definite quantities, after which the volume was made to 100 cc. by water and filtered. The residue was not washed. Aliquot parts of the filtrate were titrated with N/100 sodium hydroxide, using phenolphthalein as indicator. The difference between the amount of acid added and that found in the filtrate represents the amount of acid combining with the casein, plus the amount adhering mechanically to the casein. It was necessary to use dilute solutions of acid in order to avoid dissolving the proteid by an excess of acid. The materials used in this work were the 4 preparations of base-free casein which have already been described on p. 471.

Amount of Acid Used Kept Constant in Relation to Proteid.—In the experiments, the results of which are given below in Table I., we used different solutions of hydrochloric acid of varying dilution, but varied the quantity so that the same absolute amount of acid was used in each case, which was equal to 20 cc. of N/100 hydrochloric acid for 1 gram of base-free casein. The work was carried on at 17°–18°.

Amount of Acid Used Varying in Relation to Proteid.—In another set of experiments we used varying quantities of acid for 1 gram of proteid. Otherwise the operation was carried out like those preceding. The results are given in Table II.

Amount of Acid and Amount of Dilution Varied in Relation to Proteid.—The amount of water, in which the solid, base-free casein was suspended, was relatively considerable in the preceding experiments. We wished to see what difference, if any, there might be when we treated the casein directly with acid of varying strength and without further dilution. We suspended 1 gram of the base-free casein in each of the following amounts of hydrochloric acid: 50 cc. N/200, 40 cc. N/100, 30 cc. N/80, and 20 cc. N/60. The mixtures were allowed to

Table I.—Amount of Hydrochloric Acid Neutralized by One Gram of Base-Free Casein with Constant Amount of Acid.

No. of cc. of acid used.	Strength of acid used.	Preparation 1.		Preparation 2.		Preparation 3.		Preparation 4.	
		N/100 HCl in filtrate.	N/100 HCl in filtrate.	N/100 HCl in filtrate.	N/100 HCl in filtrate.	N/100 HCl in filtrate.	N/100 HCl in filtrate.	N/100 HCl in filtrate.	N/100 HCl in filtrate.
40	N/200	13.6	6.4	13.6	6.4	13.8	6.2	14.0	6.0
20	N/100	13.4	6.6	14.2	5.8	14.0	6.0	14.2	5.8
16	N/80	13.6	6.4	13.6	6.4	13.6	6.4	14.4	5.6
12	N/60	14.0	6.0	13.6	6.4	14.0	6.0	14.0	6.0
8	N/40	14.0	6.0	14.0	6.0	14.0	6.0	14.0	6.0
4	N/20	13.6	6.4	14.0	6.0	14.0	6.0	14.2	5.8
Average,		13.7	6.3	13.8	6.2	13.9	6.1	14.1	5.9

Table II.—Amount of Hydrochloric Acid Neutralized by One Gram of Base-Free Casein, the Amount of Acid Varying.

No. of cc. of acid used.	Strength of acid used.	Amount of acid used equal to N/100 HCl. cc.	Preparation 1.		Preparation 2.		Preparation 3.		Preparation 4.	
			N/100 HCl in filtrate. cc.	N/100 HCl in proteid. cc.	N/100 HCl in filtrate. cc.	N/100 HCl in proteid. cc.	N/100 HCl in filtrate. cc.	N/100 HCl in proteid. cc.		
30	N/200	15.0	8.8	6.2	9.2	5.8	8.6	6.4	8.8	6.2
20	N/100	20.0	13.6	6.4	13.2	6.8	13.4	6.6	13.6	6.4
20	N/80	25.0	19.2	5.8	19.2	5.8	19.0	6.0	19.6	5.4
10	N/60	16.6	10.8	5.8	10.6	6.0	10.8	5.8	11.0	5.6
Average,		. .	. .	6.0	. .	6.1	. .	6.2	. .	5.9

stand 1 hour with occasional agitation and were then filtered and aliquot portions of the filtrate titrated as in the preceding experiments. The results are given in Table III. :

Table III.—Amount of Hydrochloric Acid Neutralized by One Gram of Base-Free Casein, Amounts and Dilution of Acid Varying.

No. of cc. of acid used.	Strength of acid used.	Amount of acid used equal to N/100 HCl. cc.	Acid equal to N/100 HCl in filtrate. cc.	Acid equal to N/100 HCl in proteid. cc.
50	N/200	25.0	18.4	6.6
40	N/100	40.0	33.6	6.4
30	N/80	37.5	30.0	7.5
20	N/60	33.3	25.6	7.7

The results in Table III. indicate that, when we treat the base-free casein with a more concentrated acid solution, we have more acid left in the proteid. This is as we should expect under the conditions of experiment. The acid that is not recovered in the filtrate must either combine with the proteid or adhere to it mechanically. We made no attempt to wash the adherent or occluded acid from the proteid, because any thorough washing would remove some of the combined acid ; therefore, the more concentrated the acid used in treating the proteid, the more acid, as measured by titration, adhered to the proteid in addition to the fixed amount of acid that combined with it as compared with treatment with an equal volume of more dilute acid.

It is not easily conceivable that such an amount of acid as is represented by about 6 cc. of N/100 hydrochloric acid should be held only mechanically by 1 gram of casein, when we used solutions so dilute. Bearing on this point, the following additional experiments were made :

(1) We suspended a weighed amount of base-free casein in 50 cc. of water, allowed to stand 15 minutes, added N/100 hydrochloric acid at the rate of 6 cc. for 1 gram of casein and made the volume to 100 cc. with water. After filtration, the filtrate was titrated and the result showed that 5.2 cc. of N/100 hydrochloric acid had been held by 1 gram of casein.

(2) The experiment was repeated, allowing the mixture to

stand 1 hour after addition of acid. The result was the same as before.

(3) The experiment was repeated, except that we used only 4 cc. of N/100 hydrochloric acid for 1 gram of casein. The filtrate, on titrating, showed no acid, indicating that the entire 4 cc. of N/100 hydrochloric acid had been held by the casein.

These results indicate to us that 1 gram of base-free casein combines with about 0.5 cc. of N/10 hydrochloric acid and that the disappearance of acid is due to chemical union with proteid and not merely to mechanical mixture or adhesion.

The question has probably come to mind before this as to why free casein was not sooner isolated in the normal souring of milk, or in the treatment of milk by direct addition of acid; the cause can now readily be seen. Because it requires so little acid to change free casein into its acid combination, the point is quickly passed when we have any considerable proportion of free casein in the milk. In the normal souring of milk we were able to catch the change at a point where 65 per cent of the casein of the milk was in the form of free casein.¹ When we use an acid to precipitate casein from milk, an excess is added, so that we get, not the free casein, but the compound formed by its combination with acid.

Summary of Action of Acids on Calcium Casein (Milk-Casein).

—When calcium casein is treated with an acid, the first reaction is a union between the acid and the calcium combined with casein, resulting in the formation of base-free casein, a compound insoluble in water, but soluble in warm 5 per cent solution of sodium chloride and in hot 50 per cent alcohol, a compound which, when warmed, also possesses the property of being very plastic and capable of being drawn out into long, fine, silky threads. This base-free casein is identical with the compound which we formerly regarded as being a casein mono-salt of the acid used as precipitant.

When 1 gram of this base-free casein is treated with an amount of acid equivalent to about 0.5 cc. in the case of N/10 hydrochloric acid, the properties of the casein are changed, so that it is no longer soluble in warm 5 per cent salt solution and

¹ THIS JOURNAL, 32, 153 (1904).

only slightly soluble in hot 50 per cent alcohol; in addition it has lost entirely its plastic properties and the power of being drawn out into fine threads when warm. This substance we regard as resulting from the combination of acid with the base-free casein, forming a casein salt of the acid used. Our reasons for believing that there is actual chemical combination between the casein and acid are the following :

(1) When a given amount of base-free casein is treated with an acid, a quite definite and constant amount of acid appears to be neutralized. In the case of N/10 hydrochloric acid, 1 gram of base-free casein appears to combine with about 0.5 cc. of acid.

(2) The phenomenon of combination between proteids and acids appears to be very general, as shown by Cohnheim and others.¹

(3) When base-free casein is treated with an acid it undergoes a marked change in its properties.

(4) Although the combination is comparatively weak, it appears to be as strong as in the case of some quite stable inorganic salts. The fact that the acid can be completely removed by long-continued trituration with water does not constitute an argument against combination, because some well-known inorganic salts behave in the same way under similar treatment.

(5) By treating base-free casein with a given amount of acid, we prepare the compound insoluble in warm dilute salt solution and hot alcohol. By removing the acid from this substance, we obtain again the base-free casein with a restoration of its recognized properties of solubility and plasticity. Each of these compounds can be converted into the other by addition or removal of acid.

The Relation of Casein and Its Compounds to Paracasein and Its Compounds.

The coagulum formed by calcium casein, when treated with rennet enzyme, was called "Käse" by Hammarsten.² Schulze and Röse³ suggested the name "paracasein" for this

¹ *Chemie der Eiweisskörper*, pp. 106-114, 2d Ed., (1904).

² *Maly: Jahresb. d. Tierchemie*, 4, 138 (1874).

³ *Landw. Versuchs-Stat.*, 31, 131 (1884-5).

product and their suggestion has been very generally accepted. There is still, however, much confusion as to the exact application of this term, as we shall point out later.

According to Hammarsten¹ and others, the action of rennet enzyme on calcium casein of milk takes place in two distinct stages: (1) The rennet enzyme converts the milk-casein into paracasein, but there is no coagulation or visible change, the paracasein apparently remaining in the same condition as the milk-casein. In the absence of soluble calcium salts, the paracasein remains in this uncoagulated condition in the case of normal milk. (2) Coagulation or separation of curd takes place in the presence of soluble calcium salts. The conversion of milk-casein into paracasein, in the first stage, is due to the rennet enzyme alone, while the coagulation of the paracasein, in the second stage, is due to soluble calcium salts alone, in the case of normal milk. The term paracasein is commonly applied to both the coagulated and uncoagulated forms.

Just what chemical change, if any, takes place in the proteid in the conversion of calcium casein into paracasein by rennet enzyme has not been clearly demonstrated. According to Hammarsten's original theory,² by the action of rennet enzyme, the calcium casein of the milk undergoes a hydrolytic separation into two compounds: (1) A body difficultly soluble, forming the chief product and closely resembling casein in composition—*paracasein*; (2) an easily soluble, albumose-like body, called by him *whey-proteid*, produced in very small amount. Further, the paracasein has not the property of holding calcium phosphate in solution to the same extent that casein has. Hammarsten later modified these views,³ coming to the conclusion that the action of rennet enzyme rearranges the casein molecule only in a physical way. Du Claux⁴ regards casein as existing in milk in three different forms, in equilibrium with one another; this equilibrium can be easily disturbed by the action of acids or ferments. Coagulation, according to his theory, is a purely physical, mechanical change. A similar conclusion is reached by Fuld,⁵ milk coag-

¹ Maly: Jahresb. d. Tierchemie, **2**, 118 (1872); **7**, 158 (1877).

² *Ibid.*, **4**, 153 (1874).

³ Z. physiol. Chem., **28**, 114 (1899).

⁴ Compt. rend., **98**, 373.

⁵ Beiträge z. Chem. Physiol. und Pathol., **2**, 169 (1902).

ulation being regarded as a special case of the alternation between suspension and precipitation of a colloidal substance. Eugling¹ concluded, from work done by him, that acids or rennet, when added to milk, render the insoluble calcium salts soluble and more readily available for the coagulation of the proteid. De Vries and Boekhout² believe that free acid exerts a direct influence on its own account upon the coagulation of paracasein, in some way independent of the formation of soluble calcium salts. Loevenhart³ has stated that there is no chemical difference between casein and paracasein and that the observed differences in properties are due to physical changes, casein and paracasein being physical modifications of one and the same substance. According to his belief paracasein, in its solutions, exists in larger molecular aggregations than does casein.

We thus see that, while there is a wide range of opinion in regard to the relation of casein and paracasein, there is a prevailing tendency to regard these proteids, milk-casein and paracasein, as being essentially alike in composition.

It is our purpose to consider paracasein and some of its compounds in a similar manner to the discussion of casein given in the preceding pages; the topics will be taken up in the following order:

I. The relation of inorganic compounds to paracasein.

II. The relation of the salt-soluble compound of paracasein to paracasein.

III. The relation between the two series of compounds previously called paracasein mono-salts and paracasein di-salts.

IV. The relation of casein and its compounds to paracasein and its compounds.

(I.) The Relation of Inorganic Compounds to Paracasein.

In order to study paracasein in its relations to calcium and to acids, it was essential to obtain a paracasein that should be practically base-free. Preparations, made by coagulating milk with rennet and washing the coagulum, are high in ash content, containing often 4-5 per cent; moreover, such preparations still

¹ Landw. Versuchs-Stat., 31, 392 (1885).

² *Ibid.*, 55, 221 (1901).

³ Z. physiol. Chem., 41, 177 (1904).

contain the calcium originally combined in the calcium casein of the milk and are not satisfactory for such work as we desired to do. We therefore made a preparation of paracasein as follows :

Preparation of Paracasein.—To 1 liter of skim-milk we added 1.25 grams of ammonium oxalate ; the milk, after standing a short time, was filtered through paper. To 500 cc. of this filtrate we added 0.05 cc. of Hansen's rennet extract and kept the whole at a temperature of 37° , for 2 hours. A small amount of thymol was added. To show that the rennet enzyme had acted upon the calcium casein in the milk, we took 10 cc. of the treated milk, cooled to room temperature and added 2 drops of 10 per cent solution of calcium chloride. In a few minutes the milk had formed a firm coagulum, which indicated that the rennet enzyme had produced paracasein. The 500 cc. of treated milk we now diluted with 16 liters of warm distilled water and added dilute hydrochloric acid until the proteid had separated. This precipitation was accompanied by vigorous stirring to keep the solid as finely divided as possible, thus facilitating the removal of inorganic salts. After the precipitate had settled, the supernatant liquid was removed, the precipitate was filtered and then triturated with warm water and filtered, the trituration and filtering being repeated until all trace of chlorides was removed, which required 4 days. The precipitate, after removal of acid, was soluble in warm 5 per cent solution of sodium chloride and in hot 50 per cent alcohol. Finally, the preparation was washed with strong alcohol and ether and dried at 100° . This treatment greatly lessened its solubility in dilute salt solution and alcohol. It was nearly ash-free, containing 0.11 per cent and gave no test for chlorides when boiled with nitric acid and silver nitrate.

Solubility of Paracasein Preparation in Lime-Water.—The paracasein, prepared in the manner described, was soluble in lime-water, forming a solution having a dull, opalescent appearance.

Preparation of Basic Calcium Paracasein.—We dissolved about 2 grams of our paracasein preparation in lime-water and made the solution neutral to phenolphthalein by the addition of

N/10 hydrochloric acid. The solution became more milky in appearance, but no precipitation was observable. This solution was now precipitated by alcohol, filtered, washed several times with alcohol, finally with ether and dried at 100°. The preparation was insoluble in dilute salt solution and practically so in hot dilute alcohol. One gram contained a total of 0.0283 gram of calcium oxide and 0.0063 gram of chlorine (equivalent to 0.0047 gram of calcium oxide combined as calcium chloride). Deducting the calcium oxide equivalent, present as chloride, from the total, we have 0.0236 gram, which represents the amount of calcium oxide combined with the proteid, or 2.36 per cent. This preparation, therefore, corresponds very closely in its calcium content with the basic calcium casein. As in the case of the calcium casein preparations, all those of calcium paracasein contained calcium chloride.

Preparation of Neutral Calcium Paracasein.—When we treat a lime-water solution of paracasein with an amount of acid sufficient to turn blue litmus red, or just a little short of this, the proteid separates as a precipitate and this occurs before all the calcium of the original lime-water solution has been neutralized. This product is insoluble in dilute salt solution and nearly insoluble in hot dilute alcohol; it was thrown on a filter and washed several times with water. Filtration was rather slow. The precipitate was then washed with alcohol and ether and dried at 100°. One gram contained 0.0391 gram of ash, a total lime content of 0.0194 gram of calcium oxide and 0.0064 gram of chlorine (equivalent to 0.0048 gram of calcium oxide combined as calcium chloride). Deducting the calcium oxide equivalent, present as chloride, from the total calcium oxide, we have 0.0146 gram, which represents the amount of calcium oxide combined with the proteid, or 1.46 per cent. This preparation, therefore, corresponds closely to the neutral calcium casein.

We have seen above that the neutral calcium paracasein, formed by making a lime-water solution of paracasein neutral to litmus, by acid, separates as a precipitate, while neutral calcium casein does not separate thus. At the point of neutrality with litmus, the body formed, that is, neutral calcium

paracasein, is precipitated. *In this respect and in this respect only, does there appear to be a marked difference between the properties of casein and paracasein compounds.* This is in harmony with what takes place when rennet acts on milk, in the presence of soluble calcium salts—an insoluble calcium paracasein is formed. It shows that our preparation of paracasein had not reverted to casein.

Preparation of Base-Free Paracasein.—In 50 cc. of lime-water, requiring 21.1 cc. of N/10 hydrochloric acid for neutralization, we dissolved 0.5 gram of our ash-free paracasein. The solution became neutral to phenolphthalein after the addition of 16.9 cc. of N/10 hydrochloric acid. This leaves calcium oxide equivalent to 4.2 cc. of N/10 hydrochloric acid as combined with the proteid, or 0.01176 gram of calcium oxide, which is 2.35 per cent of the paracasein and this is the basic calcium paracasein.

When 18 cc. of N/10 hydrochloric acid had been added a precipitate began to form, but the solution was still alkaline to litmus. When 18.5 cc. of the acid had been added, precipitation was complete. This leaves calcium oxide equivalent to 2.6 cc. of N/10 hydrochloric acid as combined with the proteid, or 0.00728 gram of calcium oxide, which is 1.46 per cent of the paracasein, and this is the neutral calcium paracasein.

When 21.1 cc. of N/10 hydrochloric acid had been employed, an amount necessary to neutralize exactly the lime-water used for dissolving the paracasein, the proteid was still precipitated. It was now quite easily soluble in warm 5 per cent salt solution and nearly so in hot 50 per cent alcohol. On warming, the precipitate settled on the bottom of the beaker and was easily gathered in a mass, on a stirring rod. This mass was very plastic, showing a tendency to flow when kept warm; it also possessed the property of being drawn into long, fine, silky threads. It behaved in every respect like *base-free casein*.

In another experiment we dissolved 1.5 grams of our paracasein preparation in lime-water and then exactly neutralized the solution with N/10 hydrochloric acid. The precipitated proteid was washed with alcohol and ether and dried at 100°. Determinations of calcium and chlorine showed their presence

in the proportions found in calcium chloride, which was probably held in the proteid mass mechanically.

Behavior of Lime-Water Solutions of Paracasein Compounds toward Rennet and Soluble Calcium Salts—Basic calcium paracasein, prepared by dissolving base-free paracasein in lime-water and making neutral to phenolphthalein, is not coagulated by rennet in the presence or absence of soluble calcium salts. However, a solution of basic calcium paracasein may be coagulated on warming, by soluble calcium salts alone, without rennet.

Neutral calcium casein, prepared by dissolving base-free paracasein in lime-water and making neutral to litmus, is coagulated readily at room temperature, or on warming, by soluble calcium salts, with or without rennet, but not in the absence of soluble calcium salts.

Rennet changes calcium casein to calcium paracasein, but does not coagulate the proteid. Soluble calcium salts coagulate neutral calcium paracasein and the action takes place through quite a wide range of temperature, while basic calcium paracasein is coagulated by soluble calcium salts only after warming. Here, as in the case of the corresponding calcium casein compounds, the coagulation may be the result of purely physical change, or there may be a loose combination between the soluble calcium salt and the calcium paracasein compound.

Summary of Results of Work Done on Paracasein and Its Compounds.—We have made and studied the following paracasein preparations: (1) Base-free paracasein, the free proteid; (2) basic calcium paracasein, containing about 2.40 per cent of calcium oxide; (3) neutral calcium paracasein, containing about 1.50 per cent of calcium oxide.

(II.) *The Relation of the Salt-Soluble Compound of Paracasein to Paracasein.*

Of the three paracasein preparations made and studied by us, we have found only one that was readily soluble in warm 5 per cent salt solution and hot 50 per cent alcohol and this was the base-free paracasein. This body, on warming, showed the peculiar plastic property and the power of being drawn into

long, fine, silky threads, which are shown by the salt-soluble substance, prepared by us from cheese-curd and cheese. This is the body which our former work led us to regard as a compound formed by combination of paracasein and lactic acid, in the case of cheese and which we regarded as paracasein monolactate. As the result of our more recent work, we believe that the compound formed by treating calcium paracasein (cheese-curd) with an amount of acid just sufficient to combine with the calcium of the calcium paracasein, in addition to certain inorganic salts held mechanically in the cheese-curd, is not paracasein monolactate but base-free paracasein, or calcium paracasein, from which calcium has been removed by its combination with acid.

(III.) *The Relation between the Two Series of Compounds Previously Called Paracasein Mono-Salts and Paracasein Di-Salts.*

When to base-free paracasein we add dilute acid, another body appears to be formed, which differs in properties from the base-free proteid in being insoluble in warm 5 per cent salt solution and hot 50 per cent alcohol and also in possessing none of the peculiar plastic and ductile properties of the base-free paracasein. This substance is formed when milk is treated with rennet enzyme and allowed to coagulate, either by spontaneous souring or by direct addition of dilute acids. We at first regarded the compound as a paracasein di-salt of an acid, but since we have shown that what we regarded as a paracasein mono-salt is the base-free proteid, paracasein, we now regard this compound as resulting from the combination of acid with the base-free paracasein, forming a paracasein salt of the acid used, corresponding to the casein salts of acids, which have been already discussed.

In each of several experiments we suspended, in distilled water, portions of 0.5 gram of base-free paracasein and treated this with varying amounts of dilute acid of different strengths, agitating from time to time, for 1 hour. The mixture was filtered and the filtrate titrated with N/100 hydrochloric acid. The amount of acid not recovered in the filtrate is regarded as representing, approximately, the quantity that had combined

with the paracasein. This was found to be equivalent to about 0.5 cc. of N/10 hydrochloric acid, closely agreeing with the results obtained by treating base-free casein with acid.

(IV.) *The Relation of Casein and Its Compounds to Paracasein and Its Compounds.*

We have made preparations of the following compounds, which have been described in the preceding pages :

Casein, the base-free or uncombined proteid.

Basic calcium casein, containing the free proteid combined with about 2.40 per cent of calcium oxide.

Neutral calcium casein, containing the free proteid combined with about 1.50 per cent of calcium oxide, probably identical with casein as it exists in cows' milk.

Casein salts of acids, formed by combination of the free proteid with acids.

Paracasein, the base-free or uncombined proteid.

Basic calcium paracasein, free paracasein combined with about 2.40 per cent of calcium oxide.

Neutral calcium paracasein, free paracasein combined with about 1.50 per cent of calcium oxide, probably identical with the uncoagulated body present in cows' milk treated with rennet enzyme, in the absence of soluble calcium salts.

Paracasein salts of acids, formed by combination of the free proteid with acids.

A comparison of the properties of casein and paracasein and their compounds strongly suggests that they are chemically alike, paracasein and its combinations being larger molecular aggregations than casein and its corresponding compounds, in accordance with the suggestion of Loevenhart. The following statements serve to bring out the close resemblance more strikingly :

(1) The free proteids, casein and paracasein, possess the same solubilities in warm 5 per cent salt solution and hot 50 per cent alcohol. They possess the same peculiar plastic and ductile properties when warmed.

(2) Casein and paracasein form compounds containing the same amounts of combined calcium oxide.

(3) Casein and paracasein, when treated with dilute acid in

the proportion of 1 gram to about 0.5 cc. of N/10 hydrochloric acid, are changed into bodies having the same properties, which differ strikingly from those of the free proteids.

(4) Neither basic calcium casein nor basic calcium paracasein is coagulated by rennet, either in the presence or absence of soluble calcium salts. Both these compounds are coagulated when warmed to 35° – 45° in the presence of soluble calcium salts, but not in the absence of such salts.

(5) Neutral calcium casein (present in milk) is coagulated by a few drops of a soluble calcium salt on warming and neutral calcium paracasein (present in milk acted upon by rennet enzyme) is coagulated, at ordinary temperatures, by soluble calcium salts. Neither neutral calcium casein nor neutral calcium paracasein is coagulated by rennet in the absence of soluble calcium salts.

(6) Neutral calcium casein, prepared by making a lime-water solution of free casein neutral to litmus, is an opalescent solution, free from any visible suspended particles; neutral calcium paracasein, prepared by making a lime-water solution of free paracasein neutral to litmus, is a clearly defined coagulum. In this respect only does there appear to be any marked difference in the behavior of the neutral calcium compounds of casein and paracasein. Here the difference is one of degree rather than of kind, because neutral calcium casein is coagulated by small amounts of soluble calcium salts on warming, while neutral calcium paracasein is coagulated at lower temperatures by soluble calcium salts.

The Relation of the Salt-Soluble, Alcohol-Soluble Product in Cheese to Paracasein.

It was from our work with cheese (American cheddar) that we gained the first suggestion which led us to investigate this field. It is desirable, therefore, that we should now, if possible, establish the relation between the salt-soluble, alcohol-soluble body obtained from cheese, which we were first led to regard as paracasein monolactate and the paracasein compounds we have prepared from milk and discussed in the preceding pages.

We have established the fact that fresh cheddar cheese con-

tains a large percentage of its proteid in the form of a body soluble in warm 5 per cent salt solution and in hot 50 per cent alcohol. Weidmann¹ dissolved, from Emmenthaler cheese, by hot alcohol, a substance called by him caseoglutin. Röse and Schulze² made a quite extensive study of the properties of this compound but reached no definite conclusions as to whether it was a chemical individual or what was its relation to cheese-ripening. Winterstein³ has studied the cleavage-products of caseoglutin treated by concentrated hydrochloric acid and finds the proteid bases arginine and lysine present, in proportions differing from those obtained by Hart from casein. The results of his work cannot be regarded as conclusive, because variation of conditions in producing cleavage-products leads to quite variable results. A cleavage study made by us⁴ on a similar product suggests a close relation between casein and the salt-soluble substance, which appears to be identical with caseoglutin.

Material Used to Furnish the Preparation.—We used, as the source of our material, a cheddar cheese 1 day old, which indicated, by forming strings on a hot iron, an abundance of salt-soluble substance. Portions of the cheese were ground in sand and extracted with water at 55°. The portion insoluble in water was then divided, part to be extracted with hot 50 per cent alcohol and part with warm 5 per cent salt solution.

Preparation Made by Extraction with Alcohol.—The ground, water-extracted cheddar-curd was treated with boiling 50 per cent alcohol. The extract was filtered through paper, on a hot-water funnel. The filtrate, on cooling and standing, deposited the extracted proteid in a rubber-like mass. This was ground up in water several times, filtered, washed with 95 per cent alcohol and ether, and dried at 100°. The product was a hard mass, difficult to pulverize. It contained 1.40 per cent of ash.

Preparation Made by Extraction with 5 Per Cent Solution of Sodium Chloride.—The remaining portion of ground, water-

¹ Landw. Jahres., 1882, p. 587.

² Landw. Versuchs Stat., 31, 130 (1884-5).

³ Z. physiol. Chem., 41, 487 (1904).

⁴ THIS JOURNAL, 28, 420 (1902).

extracted cheese was extracted with a 5 per cent solution of sodium chloride, at 60°, filtered through paper twice and then precipitated with 2 volumes of 95 per cent alcohol. On standing over night the precipitate separated. It was filtered, washed by decantation with water several times to remove the salt and finally thrown on a filter-paper, washed with alcohol and ether and dried at 100°. The product was easily powdered. It contained 1.37 per cent of ash.

Behavior of Salt-Soluble and Alcohol-Soluble Preparations toward Lime-Water.

We made a study of the power of these two preparations to combine with calcium for comparison with base-free casein, in order to ascertain whether they were base-free or not. In portions of 50 cc. of lime-water, of known strength, we dissolved 0.5 gram each of base-free casein, of the salt-soluble preparation and of the alcohol-soluble preparation. These lime-water solutions of proteids were then treated with N/10 hydrochloric acid until the solution was neutral to phenolphthalein, with the following results :

Table IV.—Power of Different Preparations to Combine with Calcium.

	N/100 HCl required cc.	Difference of N/10 HCl between lime- water and solu- tions of proteids in lime-water.	Equivalent to CaO combined with proteid. Gram.	Per cent of CaO combined with proteid.
50 cc lime-water	19.5	.	. .	. .
0.5 gram of base-free casein, dissolved in 50 cc. lime- water	15.5	4.0	0.0112	2.24
0.5 gram of alcohol prepa- ration, dissolved in 50 cc. lime-water	15.4	4.1	0.01148	2.29
0.5 gram of salt-soluble preparation, dissolved in 50 cc. lime-water	15.6	3.9	0.01093	2.19

These results show that the salt-soluble and alcohol-soluble preparations, made from cheese, possessed the same power of

combining with calcium as do casein or paracasein known to be base-free and that they must, therefore, have been base-free proteids, capable of forming a calcium combination equivalent to that of basic calcium casein or paracasein. These preparations from cheese appear, therefore, to be identical with base-free paracasein.

The calcium of the ash present was evidently not a part of the proteid molecule, but was probably an impurity of calcium lactate, or possibly this salt loosely combined with the proteid, appearing, on ignition, as calcium phosphate.

Behavior of Salt-Soluble and Alcohol-Soluble Preparations toward Acids.

In determining the amount of acid that could combine with these salt-soluble and alcohol-soluble preparations made from cheese, we used the methods already employed in connection with casein and paracasein. We suspended 0.5 gram of proteid in water, added 10 cc. of N/100 hydrochloric acid, made the volume up to 100 cc., filtered and titrated the filtrate with N/100 sodium hydroxide, with phenolphthalein as indicator. The results, calculated on the basis of 1 gram of proteid, were as follows :

Table V.—Acid-Combining Power of Different Preparations.

Material used.	Amount of acid used equal to N/100 HCl.	Acid equal to N/100 HCl in filtrate.	Acid equal to N/100 HCl in proteid.
	cc.	cc.	cc.
Base-free casein	20	13.6	6.4
Alcohol-soluble preparation	20	13.6	6.4
Salt-soluble preparation	20	14.0	6.0

In respect to acid-combining power, these results indicate that the alcohol-soluble and salt-soluble preparations made from cheese are essentially the same compounds as casein and paracasein, that is, they are essentially base-free paracasein.

The Nomenclature of Casein and Paracasein and Their Compounds.

From the work presented in the preceding pages there is reason to believe that there exist the following bodies, repre-

senting milk-casein and paracasein and the compounds formed by them :

Casein, basic calcium casein, neutral calcium casein, casein salts of acids, paracasein, basic calcium paracasein, neutral calcium paracasein and paracasein salts of acids.

In most of the literature on the subject, the word casein is used indiscriminately to mean milk-casein, free casein, or those casein salts formed by acid precipitation. In many cases it is used comprehensively to include all the proteids in cows' milk. A similar state of confusion exists in regard to the use of the word paracasein. It would, therefore, seem pertinent to make the following suggestions, tentatively at least, in regard to the nomenclature of these compounds :

(1) That the compound existing in cows' milk, commonly called casein, be called calcium casein.

(2) That the word casein be applied only to the free proteid, that is, the base-free casein.

(3) That the casein compound containing about 2.40 per cent of calcium oxide be called basic calcium casein.

(4) That a compound formed by precipitation and combination with an acid be called a casein salt of the acid used.

(5) That the same nomenclature be applied to the corresponding paracasein bodies, simply substituting the word paracasein for casein, with the following addition: The name calcium paracasein should be applied to the uncoagulated substance produced in milk by rennet enzyme, while the coagulum of this substance, caused by soluble calcium salts, should be called *coagulated* calcium paracasein.

The Relation of the Results to Certain Changes Taking Place during the Cheese-Making Process.

In the manufacture of cheddar and similar types of cheese, after the addition of rennet enzyme and coagulation, there takes place a progressive change, resulting in the production of increased amounts of a proteid soluble in warm 5 per cent solution of sodium chloride. This product may amount, in fresh cheese, to 75-80 per cent of the proteids present. We were led by the former work to interpret these facts as follows: Lactic acid, formed by the lactic fermentation of milk-

sugar, combines with the paracasein of the curd, forming paracasein monolactate, insoluble in water but soluble in warm 5 per cent salt solution and in hot 50 per cent alcohol. In the light of the results of our more recent work, this interpretation must be modified and the observed facts appear to be explained correctly in the following manner: The coagulum following the addition of rennet enzyme to milk is calcium paracasein, either mixed or loosely combined with soluble calcium salts. While lactic acid is being formed in the cheese-making process, it combines with the calcium of the calcium paracasein, forming free paracasein and calcium lactate. The conditions of manufacture are so controlled that, normally, not enough is produced to convert all the calcium paracasein to base-free paracasein. The proteids of the curd are, therefore, a mixture, in varying proportions, of calcium paracasein and free paracasein. It is the free paracasein that is soluble in warm 5 per cent salt solution and in hot 50 per cent alcohol; and it is this body that has the characteristic property of being drawn out in fine, silky threads, when touched with a hot iron. It is the free paracasein that imparts to cheese-curd its peculiar plastic and ductile properties, exhibited in the process known as "packing" or "matting." It is the free paracasein, therefore, that appears to be the substance in which the various chemical changes grouped under the general term of cheese-ripening begin to take place.

When, in the process of cheese manufacture, an excess of lactic acid is produced, 0.7-0.8 per cent, we have the product familiarly known as cottage or Dutch cheese. It has a loose, granular structure and is insoluble in warm 5 per cent salt solution. In this case all the calcium of the calcium paracasein combines with lactic acid, after which additional amounts of free lactic acid formed unite, in a loose combination, with the free paracasein, producing paracasein lactate, which differs from free paracasein in a most marked manner in respect to its solubilities in dilute salt solution and hot alcohol and in its plasticity and ductility.

Summary.

1. *Object.*—The primary object of the work presented is to

make a further study of the casein and paracasein salts of acids,¹ with an extension to the free proteids and some of their combinations with bases.

2. *Base-free Casein*.—Preparations of casein free from ash, or nearly so, were made by precipitating dilute skim-milk with acids, removing the acid and inorganic matter by repeated filtration and trituration with water in a mortar. The process required several days.

3. *Basic Calcium Casein*.—Compounds were made of base-free casein in which the proteid combined with about 2.40 per cent of calcium oxide. One such preparation was made by triturating together calcium carbonate and the base-free casein, suspended in water and another by dissolving base-free casein in lime-water and making this neutral to phenolphthalein by acid.

4. *Neutral Calcium Casein*.—By treating base-free casein, dissolved in lime-water, with acid until the liquid is almost neutral to litmus, there is formed a compound of casein and calcium oxide containing about 1.50 per cent of calcium oxide.

5. *Calcium Casein Compounds in Relation to Rennet Enzyme and Soluble Calcium Salts*.—Rennet enzyme coagulates neither neutral nor basic calcium casein. Neutral calcium casein, after treatment with rennet, is coagulated at ordinary temperatures by soluble calcium salts. Soluble calcium salts, such as calcium chloride, coagulate both neutral and basic calcium casein on warming to 35°–45°.

6. *Casein Present in Milk as Neutral Calcium Casein*.—In its behavior toward soluble calcium salts on warming and at ordinary temperatures, after treatment with rennet, neutral calcium casein behaves like milk-casein and casein is probably present in cows' milk as the neutral calcium casein.

7. *Identity of Base-Free Casein and the Salt-Soluble Proteid*.—A base-free casein, prepared either directly from milk or by treating a lime-water solution of free casein with an acid to the point of acidity with litmus, is readily soluble in warm 5 per cent salt solution and in hot 50 per cent alcohol. This body, when freshly prepared and sufficiently warmed, is very plastic

¹ THIS JOURNAL, 28, 411 (1902).

and ductile. It behaves, in all respects, like the substance which we were formerly led to regard as a compound formed by combination of casein and an acid and which we regarded as a casein mono-salt of the acid precipitant.

8. *Relation between the Two Series of Compounds Previously Called Casein Mono-Salts and Casein Di-Salts of Acids.*—When 1 gram of base-free casein is treated with about 0.5 cc. of N/10 hydrochloric acid, a substance is formed which is insoluble in warm 5 per cent salt solution and in hot 50 per cent alcohol and which is no longer plastic or ductile on warming. This is like the substance usually formed when milk coagulates by natural souring. By treating base-free casein with dilute acid, it was found that 1 gram of base-free casein appears to combine with about 0.5 cc. of N/10 hydrochloric acid, forming a casein salt of hydrochloric acid. While the compounds formerly regarded by us as casein mono-salts of acids have been shown by us to be identical with base-free casein, the compounds which we called casein di-salts of acids are compounds formed by combination of acids with free casein.

9. *Paracasein and Its Compounds.*—A preparation of base-free paracasein was made and from this, dissolved in lime-water, were prepared (1) basic calcium paracasein, containing in combination about 2.40 per cent of calcium oxide, (2) neutral calcium paracasein, containing about 1.50 per cent of combined calcium oxide.

10. *Comparison of Properties of Casein and Paracasein and Their Compounds of Calcium.*—Basic calcium casein and paracasein appear to be soluble in water, forming slightly opalescent solutions. Neither is coagulated by rennet, but both are precipitated by soluble calcium salts on warming. Neutral calcium casein is coagulated by soluble calcium salts on warming to 35°-45°, but not at ordinary room temperatures, while neutral calcium paracasein is completely and quickly coagulated, at room temperatures, by soluble calcium salts. Free casein and free paracasein, freshly prepared, possess the same solubilities in warm 5 per cent salt solution and in hot 50 per cent alcohol; they also possess the same characteristic properties of plasticity and ductility. The close resemblance of casein and

its compounds to paracasein and its compounds, respectively, suggests that they are chemically alike, paracasein being different only by consisting of a larger molecular aggregation than casein.

11. *Relation of Paracasein to Salt-Soluble Substances and to Compounds Formed by Treatment with Acid.*—Free paracasein appears to be identical in characteristic properties with the compounds we formerly called paracasein mono-salts of the acids used as precipitants. The compounds which we have heretofore called paracasein di-salts of acids appear to be combinations of free paracasein and the acids used as precipitants, 1 gram of paracasein uniting, for example, with about 0.5 cc. of N/10 hydrochloric acid.

12. *Relation of the Salt-Soluble Product of Cheese to Paracasein.*—From water-extracted, fresh cheddar cheese we prepared one extract by warm 5 per cent salt solution and another by hot 50 per cent alcohol. These preparations have, in common with free paracasein, the characteristic properties of plasticity and ductility and the same combining power with bases and acids, they therefore appear to be free paracasein instead of paracasein monolactate, as we were formerly led to believe.

13. *Chemical Changes in Calcium Casein Resulting from Souring of Milk or Addition of Acids.*—When an acid is formed in cows' milk, or added to it, the acid first combines with the bases of some of the inorganic salts of the milk and then with the calcium that is combined with the casein, resulting in the formation of a precipitate which is free casein. By further formation, or addition of acid, the free casein unites with it, forming a casein salt of the acid, this compound, in the case of lactic acid, being the coagulum familiar in the ordinary souring of milk.

14. *Chemical Changes in Calcium Paracasein during the Process of Making Cheddar Cheese.*—The coagulum, following the addition of rennet enzyme to milk, is calcium paracasein, either mixed or loosely combined with soluble calcium salts. While lactic acid is being formed in the process of cheese-making, it combines with the calcium of the calcium paracasein, forming free paracasein and calcium lactate. It is this

free paracasein, thus formed, that is soluble in warm dilute salt solution and in hot 50 per cent alcohol and possesses characteristic properties of plasticity and ductility.

15. *Suggestions in Regard to the Nomenclature of Casein and Paracasein and Their Compounds.*—Much confusion prevails, at present, in the use of the terms casein and paracasein. It is suggested that the following nomenclature be used: (1) That the compound existing in cows' milk be called calcium casein. (2) That only the free proteid be called casein. (3) That the casein compound containing 2.40 per cent of calcium oxide be called basic calcium casein. (4) That a compound formed by precipitation and combination with acid be called a casein salt of the acid used. (5) That the same nomenclature be applied to the corresponding paracasein bodies, with the following addition: Calcium paracasein should be applied to the uncoagulated form and the term *coagulated* calcium paracasein to the coagulated form.

GENEVA, N. Y.,
Dec., 1904.

Contributions from the Chemical Laboratory of Harvard College.

NOTE ON THE PREPARATION OF CERTAIN AMINES.

BY LATHAM CLARKE.

In the course of a research¹ on addition compounds formed from dimethylaniline and allied substances, it was necessary to have moderately large quantities of several dialkylated amines. In preparing these I have worked out a process which is more convenient than the older methods and gives a much larger yield; for example, this method gave, with *o*-toluidine and methyl iodide, a practically quantitative yield of dimethylorthotoluidine and with *p*-toluidine and methyl iodide gave 76–79 per cent of the theoretical yield of dimethylparatoluidine. By Thomsen's method,² on which mine was founded, not over 30 per cent was obtained in any case.

I have also succeeded in improving the method for making benzylamine, so that, in a single case, from 100 grams of

¹ Jackson and Clarke: Ber. d. chem. Ges., 37, 176.

² Ber. d. chem. Ges., 10, 1586.

benzyl chloride I obtained 40 grams of this substance instead of the 25 grams yielded by Mason's¹ original process.

The dimethyltoluidines have been prepared by two methods, Thomsen's² and Nölting's.³ Thomsen's method consists in treating the amine repeatedly with methyl iodide and caustic soda, forming the trimethyltolylammonium iodide and this, by treating with lead oxide, yields the hydrate, which is subjected to distillation, several steps thus being involved, the last a somewhat wasteful one. Nölting seals up the amine in a tube with methyl alcohol and hydrochloric acid, heats the mixture for 2 days at 200°–220° and then rectifies the product. Both these methods are somewhat tedious and the yields are not especially good.

It is best to illustrate my general method by a specific experiment. Ten grams of *p*-toluidine were treated with 75 grams of methyl iodide (approximately 5 times the necessary amount) in a round-bottomed flask, with a very long return-condenser attached. This was placed on a water-bath, at 50°, and the violent boiling which soon began was allowed to continue 30–40 minutes, shaking occasionally to prevent caking. The excess of methyl iodide was then distilled over the water-bath and, when practically all had been driven off, the white pasty residue was treated with an equal volume of water, which dissolved all but the small amount of methyl iodide left; by warming the liquid and passing a stream of air through it this was soon removed entirely. It is almost impossible to get out all the iodide by simple heating, but the success of the method depends on its complete removal. To the clear, somewhat colored liquid remaining a strong solution of potassic hydrate was then added and the floating, oily layer separated and dried with solid caustic potash.

After drying, the oil was subjected to another treatment with methyl iodide under the same conditions as before, the boiling being continued rather longer. The excess of iodide was distilled off, the residue dissolved in water and the last traces of iodide expelled as before. On treating with alkali

¹ J. Chem. Soc., 63, 1313.

² Ber. d. chem. Ges., 10, 1586.

³ *Ibid.*, 11, 2279.

this time, the oil which separated generally sank to the bottom and was removed and dried over solid caustic potash. It was then distilled, when pure dimethyl paratoluidine passed over as a clear, colorless liquid, boiling at 183° (760 mm.). The yield was 10 grams, or 79.3 per cent of the theoretical.

The purity of the dimethylorthotoluidine and dimethylparatoluidine, obtained in this way, was proved by their constant boiling-points, halogen tests, which gave satisfactorily negative results and determinations of nitrogen (Dumas) :

0.2345 gram ortho gave 22.0 cc. N at 24° and 760 mm.

	Calculated for $C_9H_{13}N$.	Found.
N	10.37	10.51

0.3511 gram para gave 33.2 cc. N at 24° and 760 mm.

	Calculated for ~~$C_9H_{13}N$~~	Found.
N	10.37	10.60

*see errata
p. 647*
This method has several obvious advantages over Thomsen's or Nölting's. The excess of iodide has so kept down the temperature that there is no elimination of hydriodic acid before the treatment with alkali; before the alkali is added all methyl iodide is removed, thus preventing the formation of any trimethyltolylammonium iodide as a by-product. The great excess of methyl iodide also prevents any toluidine or methyltoluidine from remaining unchanged and the process is not wasteful, because almost all the excess can be saved and used again. The reaction is, therefore, made almost an exact one.

Using isoamylamine, methylisoamylamine and dimethylisoamylamine were prepared by this method, both for the first time. Methylisoamylamine is a clear, colorless liquid, with a peculiar, not unpleasant odor, it boils at 95° (758 mm.). From this the dimethylisoamylamine was made, which is also a clear, colorless liquid with a strong odor, boils at 98° (758 mm.), it gave the right percentage of nitrogen (Dumas), but, unfortunately, the record of the analysis is lost. In their preparation the reactions with methyl iodide are very violent and it was found best to use about 10 times the calculated

amount of the latter in each case. The temperature at which the excess of methyl iodide was driven off was not allowed to exceed 50° . Although the reaction proceeds well, yet lack of experience and the small quantities worked with caused the yields to be not very good, only about 40 per cent of the theoretical amount of dimethylisoamylamine being obtained.

Dimethylbenzylamine was prepared by this method very easily; it has been previously made by Jackson and Wing,¹ by the action of dimethylamine on benzyl chloride. The benzyl amine used in this work was obtained by a modification of Mason's method,² which proved successful the first and only time it was tried. Mason used a 15 per cent solution of ammonia in absolute alcohol and so much benzyl chloride that, approximately, 20 molecules of ammonia were present to 1 of benzyl chloride. This was allowed to stand 5 days and then the separation of the primary, secondary and tertiary amines formed in the reaction was proceeded with. In this manner 100 grams of benzyl chloride gave 25 grams benzylamine, 30 grams dibenzylamine and 6 grams tribenzylamine.

Like Mason, I used a practically saturated ammonia solution in absolute alcohol and the same proportion of ammonia to benzyl chloride, but in my case the benzyl chloride was dropped slowly from a separating-funnel and a Witt stirrer was made use of in such a way that the drops, as they entered, were violently torn apart and stirred deeply in, thus preventing the outer part of the drop, which had already reacted with the ammonia, from reacting with the inner part, which had not. The dropping was continued for 6 hours and the whole was then allowed to stand 3 days, when the amines were separated according to Mason's method. From 100 grams of benzyl chloride, 40 grams of benzylamine, 16 grams of di- and 4 grams of tri-benzylamine were obtained.

From benzylamine a 40 per cent yield of dimethylbenzylamine was obtained which boiled at 185° (760 mm.) The methylbenzylamine was isolated and boiled at 175° (760 mm.). The reaction here with the methyl iodide is very violent, like

¹ THIS JOURNAL, 9, 79 (1887).

² J. Chem. Soc., 63, 1313.

that with isoamylamine and similar proportions of amine to methyl iodide were used.

α - and β -naphthylamines do not add methyl iodide readily enough to make this method applicable. When α - and β -dimethylnaphthylamines were desired they were obtained by the methods of Friedländer and Holman¹ and Hantzsch,² respectively.

Contributions from the Chemical Laboratory of Harvard College.

THE DETERMINATION OF OXALIC ACID BY PERMANGANATE IN THE PRESENCE OF HYDROCHLORIC ACID.

BY GREGORY PAUL BAXTER AND JOAQUIN ENRIQUE ZANETTI.

The use of potassium permanganate as an oxidizing agent, in the presence of hydrochloric acid, has been the subject of frequent investigations which have made it certain that, in the oxidation of ferrous iron, there is invariably a loss of chlorine from the liquid unless manganous salts, phosphoric acid, or both are added to the ferrous solution, before titration. The determination of oxalic acid by permanganate, in the presence of hydrochloric acid, has received less attention. Zimmermann³ concluded that hydrochloric acid does not interfere with the titration, but upon the basis of analyses where only 20 cc. of permanganate were employed and the volume determined only to tenths of a cc. Fleischer⁴ makes the same statement. The various reference books upon quantitative analysis almost universally prescribe the addition of manganous salts to prevent loss of chlorine. Ostwald,⁵ on the other hand, states that oxalic acid may be titrated with perfect sharpness, in the presence of hydrochloric acid, without a trace of chlorine being set free. Finally, Gooch and Peters⁶ have shown conclusively that the process is an accurate one if a manganous salt is added

¹ Ber. d. chem. Ges., **21**, 3124 (1888).

² *Ibid.*, **13**, 1348.

³ Ann. Chem. (Liebig), **213**, 305 (1882).

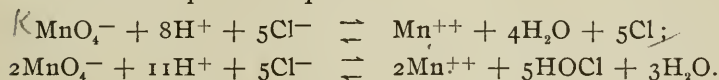
⁴ Vol. Anal., Trans. Muir, 1877, p. 71.

⁵ Foundations of Analyt. Chem., p. 151.

⁶ Am. J. Sci., **7**, 461 (1899).

previously to titration, but their results, in cases where manganous salts were not employed, show a positive error in the quantity of permanganate necessary to complete the oxidation. However, in their experiments, the hydrochloric acid was added to solutions which already contained 10 cc. of approximately 50 per cent sulphuric acid, so that the acid concentration was much higher than that which usually exists in an analysis.

A study of the mechanism of the reaction by which chlorine is liberated by the permanganate, leads to the conclusion that the initial factors are the permanganate, hydrogen and chlorine ions, which unite in proportions, by numbers, indicated by one of the two possible equations:



According to either of these equations the reaction should be most susceptible to variations in the concentration of the hydrogen ion, somewhat less so to the concentration of the chlorine ion and least to that of the permanganate ion. If, then, the concentration of the hydrochloric acid is reduced to as low a value as is compatible with the rapid oxidation of the oxalic acid, it should be possible at least to minimize the loss of chlorine. The first experiments were directed to test this point.

A solution of potassium permanganate was prepared, containing about 4 grams in a liter. A solution of recrystallized oxalic acid contained about 12 grams per liter. First the strength of the permanganate was very carefully determined, by titration against 25 cc. portions of the oxalic acid solution, in the presence of sulphuric acid. After the relation between the permanganate and oxalic acid solutions had been accurately established, titrations were performed with the use of 10 cc. of dilute hydrochloric acid (sp. gr. 1.04+) for each 25 cc. portion of the oxalic acid, which was diluted to 150 cc. before titration. It was soon found that the volume of permanganate necessary depended upon the *temperature of the solution* during the titration. If the temperature was at or above 70° at the beginning of the titration, decolorization began as soon as a few cc. of the permanganate had been added and the results agreed exactly with those obtained by the use of sulphuric

acid instead of hydrochloric acid. On the other hand, if the temperature of the oxalic acid solution was below 70° , it was necessary to add more permanganate before the reaction visibly began and more permanganate was necessary to complete the oxidation. Furthermore, the solution had the peculiar odor of hypochlorous acid,¹ in all cases where more than the theoretical amount of permanganate was necessary. This hypochlorous acid was apparent only before the decolorization commenced and while it was proceeding. Beyond this point, *i. e.*, as soon as the decolorization of the permanganate took place as fast as the solution was introduced, no odor of hypochlorous acid or chlorine could be detected. Whenever the hypochlorous acid was produced, 15–30 cc. of the permanganate and at the lowest temperatures even more, were necessary for the first signs of reaction. The end-point was sharp in all cases. In the following table are given the results of the first series of experiments :

Table I.

H ₂ C ₂ O ₄ . cc.	HCl. cc.	Volume. cc.	Temperature at beginning.	KMnO ₄ used. cc.	Theoretical KMnO ₄ . cc.	Error in per cent.
25	10	150	$80^{\circ} \pm$	45.72	45.74	—0.04
"	"	"	$80^{\circ} \pm$	45.74	"	0.00
"	"	"	$80^{\circ} \pm$	45.73	"	—0.02
"	"	"	$80^{\circ} \pm$	45.74	"	0.00
"	"	"	70°	45.74	"	0.00
"	"	"	70°	45.77	"	+0.07
"	"	"	65°	45.79	"	+0.11
"	"	"	60°	45.78	"	+0.09
"	"	"	50°	45.82	"	+0.18
"	"	"	40°	45.97	"	+0.50

It is probable that the action of the permanganate upon the hydrochloric acid, at low temperatures, produces, primarily, hypochlorous acid, which is slightly dissociated and readily volatile. That no appreciable amount of hypochlorous acid is formed at high temperatures may be due to more rapid removal, under these conditions, of either the permanganate or the hypochlorous acid by reaction with some other substance. The removal of the former may be due to the fact that potassium permanganate reacts more vigorously at high than at low

¹ If a solution of potassium permanganate is warmed to 40° with dilute hydrochloric acid, the odor of hypochlorous acid is very marked and a precipitate of manganese dioxide is formed.

temperatures with manganous salts, according to Guyard's reaction, to form a compound of trivalent or quadrivalent manganese, which, in turn, is capable of rapidly oxidizing oxalic acid.¹ Since manganous salts are produced by the reduction of the permanganate, in titrating with permanganate, in the presence of hydrochloric acid, at high temperatures the Guyard reaction is accelerated to such an extent that the concentration of the hypochlorous acid is kept at a minimum, while the effect of cooling during titration is counterbalanced by the accumulating manganous salt. Obviously the temperature *at the beginning* of the titration, while the concentration of the manganous salt is low, is the important factor. In the presence of large quantities of manganous salt, as Gooch and Peters have pointed out,² the Guyard reaction is so much accelerated that exact results may be obtained even at 25°.

Possibly, however, an additional effect of high temperatures is to accelerate the reaction between the hypochlorous and hydrochloric acids to form chloride, which is readily taken up by oxalic acid, or that between hypochlorous acid and manganous salts to form manganese dioxide which then oxidizes the oxalic acid.

After showing the effect of temperature upon the reaction it was interesting and desirable to determine the influence of varying other conditions. In Table II. are given the results of different dilutions:

Table II.

H ₂ C ₂ O ₄ . cc.	HCl. cc.	Volume. cc.	Temperature at beginning.	KMnO ₄ used. cc.	Theoretical KMnO ₄ . cc.	Error in per cent.
25	10	50	80°±	45.78	45.74	+0.09
"	"	50	80°+	39.53	39.50	+0.08
"	"	50	80°+	39.52	39.50	+0.05
"	"	100	80°±	45.78	45.74	+0.09
"	"	100	80°+	39.46	39.50	-0.10
"	"	100	80°+	39.50	39.50	0.00
"	"	100	80°+	39.48	39.50	-0.05
"	"	300	75°	45.73	45.74	-0.02
"	"	300	58°	45.81	45.74	+0.15
"	"	300	45°	45.96	45.74	+0.48

¹ Shilow: Ber. d. chem. Ges., 36, 2735 (1903). Strabal: Z. anorg. Chem., 42, 1 (1904).

² Loc. cit.

It is evident that varying the concentration, within wide limits, has no appreciable effect, but, that as before, the temperature is an extremely important factor.

A stronger solution of potassium permanganate was found to act no differently from those first employed, thus bearing out the conclusion, previously expressed, that the concentration of the permanganate ion has a comparatively slight influence. In the starred analyses the permanganate was added slowly at first, until the reaction was well started. This method of procedure is seen to have had a beneficial effect. The temperature, below which an error is introduced in the case of the more concentrated permanganate also, is very close to 70° (Table III.):

Table III.

H ₂ C ₂ O ₄ . cc.	HCl. cc.	Vol- ume. cc.	Temperature at beginning.	KMnO ₄ used. cc.	Theoretical KMnO ₄ . cc.	Error in per cent.
25	10	150	80°	21.68	21.70	—0.09
"	"	"	80°	21.70	"	0.00
"	"	"	90°	21.70	"	0.00
"	"	"	90°	21.68	"	—0.09
"	"	"	75°	21.70	"	0.00
"	"	"	75°	21.70	"	0.00
"	"	"	70°	21.70	"	0.00
"	"	"	70°	21.72	"	+0.09
"	"	"	70°	21.71	"	+0.05
"	"	"	70°	21.70*	"	0.00
"	"	"	65°	21.72	"	+0.09
"	"	"	65°	21.70*	"	0.00
"	"	"	65°	21.70*	"	0.00
"	"	"	60°	21.74	"	+0.18
"	"	"	60°	21.72	"	+0.09
"	"	"	60°	21.77	"	+0.32
"	"	"	60°	21.77*	"	+0.32
"	"	"	60°	21.77*	"	+0.32
"	"	"	60°	21.74*	"	+0.18
"	"	"	60°	21.74*	"	+0.18
"	"	"	55°	21.81	"	+0.51
"	"	"	55°	21.74*	"	+0.18

Next the effect of increasing the concentration of the hydrochloric acid only was investigated and it was found that a

slight positive error, which increased with the concentration of the hydrochloric acid and diminished with the temperature, was introduced (Table IV.). In the last analysis the end-point, though sharp, soon faded :

Table IV.

H ₂ C ₂ O ₄ . cc.	HCl. cc.	Volume. cc.	Temperature at beginning.	KMnO ₄ used. cc.	Theoretical KMnO ₄ . cc.	Error in per cent.
25	20	150	80°±	45.83	45.74	+0.20
"	20	"	85°	21.69	21.70	-0.05
"	20	"	75°	34.94	34.93	+0.03
"	20	"	85°	34.94	34.93	+0.03
"	20	"	80°	34.94	34.93	+0.03
"	30	"	80°±	45.78	45.74	+0.09
"	30	"	65°	45.80	45.74	+0.13
"	30	"	95°	21.74	21.70	+0.18
"	40	"	60°	45.86	45.74	+0.26
"	50	"	75°	45.84	45.74	+0.22
"	50	"	95°	21.73	21.70	+0.13

Finally, the concentration of the chlorine ion was varied by adding sodium chloride to the oxalic acid solution :

Table V.

H ₂ C ₂ O ₄ . cc.	HCl. cc.	Volume. cc.	Tempera- ture at be- ginning.	NaCl added. Grams.	KMnO ₄ used. cc.	KMnO ₄ theory. cc.	Error in per cent.
25	10	150	80°	3	39.48	39.50	-0.05
"	"	"	80°	3	39.47	39.50	-0.07
"	"	"	80°	5	39.50	39.50	0.00

In order to show that no oxalic acid is either volatilized or decomposed at high temperatures, in two cases titrations, in the presence of sulphuric acid, were carried out with portions which had been heated with the sulphuric acid at 88°-90°, in an open beaker, for 15 and 30 minutes, respectively. The theoretical amount of permanganate necessary was 21.70 cc., while 21.68 cc. were used in both cases. Evidently the volatilization or decomposition of oxalic acid is negligible under ordinary conditions and the precaution of keeping the temperature of the solution below 60°, which is generally recommended in text-books, is unnecessary.

The potassium permanganate solutions which were employed

in the foregoing analyses were made by dissolving the salt in hot water and allowing the solution to stand for at least 24 hours, then decanting the clear liquid. The solutions did not come in contact with rubber or any reducing substance and their strengths were determined on the day they were used. Titrations were made by both the authors, with confirmatory results in all cases.

The main results of the research are as follows :

1. It is found that oxalic acid may be determined, with great exactness, by titration with potassium permanganate, in the presence of hydrochloric acid, if the following precautions are observed :

a. The temperature of the solution, at the beginning of the titration, must be at least as high as 70° .

b. The concentration of the hydrochloric acid must not be greater than 20 cc. of dilute acid, of sp. gr. 1.04-5, in 150 cc.

c. The solution must not be too concentrated. One hundred and fifty cc. is a suitable volume for 0.3 gram of oxalic acid.

d. The permanganate must not be added too rapidly and constant stirring is advisable.

2. A tentative explanation is proposed for the cause of the loss of chlorine from the solution and consequent use of too much permanganate when the above precautions are neglected.¹

3. It is shown that oxalic acid does not appreciably volatilize or decompose, in dilute solution, at temperatures as high as 90° .

CAMBRIDGE, MASS.,
January 12, 1905.

REPORTS.

Krafft's Work on Molecular Weight Determinations in a Vacuum.

Professor F. Krafft, of Heidelberg, has made a prolonged study of the behavior of substances of high molecular weight in a vacuum and of the evaporation-points and boiling-points of metals in a vacuum. His first publication on the subject

¹ Further evidence upon this point will be presented in a subsequent paper upon the titration of ferrous iron with permanganate, in the presence of hydrochloric acid.

appeared in 1895. A list of subsequent articles is given below;¹ the last three articles are the most important. His studies have led him to a practical method of determining the molecular weight of high molecular substances and to interesting results concerning other constants of matter. The method is based on the following observations.

The passage of matter from the solid or liquid to the gaseous state depends on two factors: first, on overcoming the force of gravity; second, on overcoming the pressure of the atmosphere.

If, by working in a nearly perfect vacuum, the factor of atmospheric pressure is eliminated, we have to deal with gravity alone and the simple quantitative relation of substances to one another, in passing into the liquid or gaseous state in a vacuum, must be regarded as functions of molecular weight. How clearly defined these relations are is shown by this example:

Hexadecane, $\text{CH}_3(\text{OH}_2)_{14}\text{CH}_3$.
Molecular weight, 226.

Height of vapor column.	Boiling-point.
65 mm.	64°
175 mm.	82°
Difference, 18°	

Dotriacontane, $\text{CH}_3(\text{CH}_2)_{30}\text{CH}_3$.
Molecular weight, 450.

Height of vapor column.	Boiling-point.
65 mm.	202°
175 mm.	238°
Difference, 36°	

Here we have two strictly analogous molecules, one of which has twice the weight of the other. To lift the heavier molecule to a given height requires just twice the heat energy required to lift the lighter molecule.

In this process each layer of vapor lifts up the layer above it and is itself cooled by this work; hence, in the upper layers, on which there is practically no more vapor pressure, we reach the temperature at which the force of gravity is just overcome. This temperature is the "*vacuum boiling-point*."

With substances of high molecular weight there is no difficulty in reading the height of the vapor column within a millimeter.

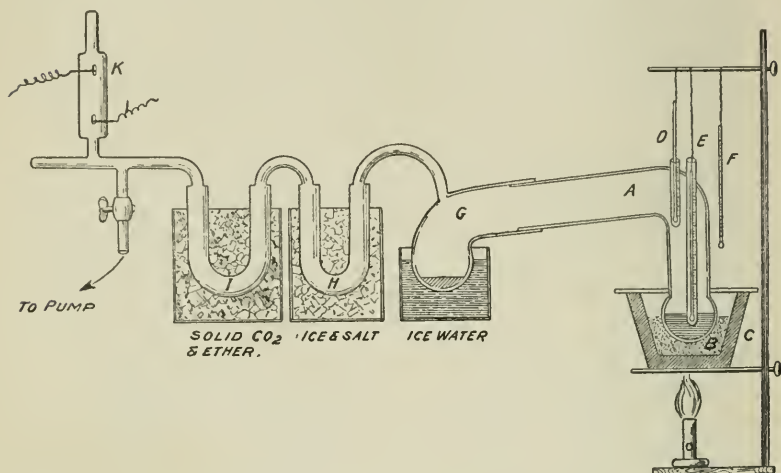
The sketch on the following page shows the apparatus used in determining molecular weight.²

To avoid, as far as possible, vapor-pressure or friction in the distilling-flask *A*, Krafft makes it in the form of a bent tube, of uniform diameter above the bulb and to avoid reading the

¹ Ber. d. chem. Ges., 28, 2583; 29, 1316, 2240; 32, 1623; 33, 3207, 3576; 35, 1690, 4339, 4344; 37, 95; 38, 242, 254, 262.

² Professor Krafft gives no drawing of his apparatus. As it is a help to understanding his method, the writer has made a diagrammatic representation from the description.

height of vapor column, he makes the flask with a uniform height of 195 mm. from the surface of the liquid substance to the bend. The bulb is partly immersed in a Wood's metal-bath, in the crucible *B*, the temperature of which is kept con-



stant by an outer crucible *C*, the space between the two iron crucibles being filled with asbestos. *D* is a thin glass tube, open at the top, fused into the flask, so that the bottom comes just below the bend; *E* is a similar tube reaching nearly to the bottom of the flask; these tubes, *D* and *E*, are the containers for the thermometers, which can be lowered in the tubes to any desired point. *F* is a thermometer, to determine the temperature of the air. A broad mica plate, bored to admit the flask, covers the bath, it protects the thermometers from radiated heat. The distilling-flask is ground into the receiver *G*, which stands in ice-water and is connected with a U-tube *H*, standing in ice and salt; this is to prevent the possible escape of vapor into the pump. A second U-tube, *I*, which can be cooled at the proper moment, by a mixture of solid carbon dioxide and ether, comes next. A tube connects the apparatus with a powerful mercury pump and the cathode light, in a Crookes-Lenard tube *K*, serves as an indicator of the vacuum.

In making a determination, the substance examined is put in the bulb of flask *A*, the apparatus connected with the pump, a current from an induction coil passed through the Crooke's tube and the substance heated by means of the metal-bath. When the bright green cathode light indicates very low pres-

sure and the substance is boiling and distilling steadily, solid carbon dioxide and ether are put in the receptacle around the U-tube *I*; this lowering of temperature lessens the pressure to such an extent that the cathode light disappears; Krafft says the pressure is less than one-millionth of an atmosphere, practically a vacuum; the pressure is now a negligible factor. The thermometers are read, which finishes the determination. $M = E \times C$; *M* is the molecular weight sought, *E* is the difference in temperature indicated by the upper and lower thermometers. *C* is a constant of the apparatus used. It depends on the height of the vapor column, the diameter of the flask, etc. and must be determined for each distilling-flask, by a trial with some substance of known molecular weight; for example, a flask tested with lauric acid ($M = 200.0$) gave

$$C = \frac{M}{E} = \frac{200.0}{22.0} = 9.009,$$

the constant for that flask.

The results tabulated below show how close the observed differences were to those calculated:

Substance.	Molecular weight.	Difference in boiling-point found.	Difference in boiling-point calculated.
<i>m</i> -Dinitrobenzene	168	17°.5	18°.6
Benzidine	184	20°.0	20°.4
Phenyl benzoate	198	20°.5	21°.9
Lauric acid	200	22°.2	22°.2
Mercury	200	22°.0	22°.2
Benzil	210	23°.5	23°.3
Palmitic acid	256	28°.5	28°.4
Nonadecane	268	30°.5	29°.7
Eicosane	282	31°.5	31°.3
Cetyl iodide	352	35°.0	39°.1
Dotriacontane	450	50°.0	50°.0

Krafft published, in 1903,¹ an interesting article on the evaporation and boiling of metals in quartz flasks. In the course of it he calls attention to the observation that, in a vacuum, evaporation precedes boiling very markedly; indeed some metals volatilize slowly, in a vacuum, several hundred degrees below their boiling-points under similar conditions and form a bright, metallic mirror on the cooler wall of the apparatus. He has taken up this work again and determined, for a number of metals, the lowest temperatures at which they evaporate in a vacuum. In experiments for this purpose it was

¹ Ber. d. chem. Ges., 36, 1690.

necessary to avoid all pressure of vapor, *i. e.*, all force of gravity. The apparatus was a horizontal glass tube 1 cm. in diameter and 25 cm. long, ground into a receiver and connected with a pump and Crookes' tube; the glass tube is closed at the far end and for 8 cm distance from the closed end the tube is surrounded by an outer tube, fused on to it, resembling the inner and outer tubes of a Liebig condenser; the space between the tubes was filled with a suitable liquid and heated, to secure an even temperature, the substance being put near the closed end of the inner tube. As noted in the table below, the evaporation-points of a few metals range from -40° for mercury to 640° for silver. The experiments with silver and other high-fusing metals were made in a tube of quartz heated in a small electric furnace.

It was shown in the first pages of this report that, in boiling in a vacuum, a vapor is formed which we may call "saturated" in relation to gravity. In boiling under a pressure of 760 mm. the vapor is "saturated" in relation to gravity plus atmospheric pressure. It would be of interest to bring these two boiling-points into measurable relation and this can be done by considering the two "limit conditions" in combination with a third "limit condition," the beginning of evaporation in a vacuum.

Mercury begins to evaporate in a vacuum at -40° and boils at 155° ; under atmospheric pressure it boils at 357° . The interval between the first and second temperatures is 195° ; the interval between the second and third is 202° ; the intervals are approximately equal; how close these relations are is shown in this table:

Element.	Beginning of evaporation in vacuum.	Boiling-point in vacuum.	Difference, I.	Boiling- point, 760 mm.	Difference, II.
Mercury	-40°	155°	195°	357°	202°
Cadmium	156°	450°	294°	749°	299°
Zinc	184°	550°	366°	920°	370°
Potassium	63°	365°	302°	667°	302°
Sodium	98°	418°	320°	742°	324°
Bismuth	270°	993°	723°	1700°	707°
Silver	680°	1360°	680°	2040°	680°

If, as shown above, the essential work during boiling in a vacuum consists in overcoming the force of gravity, then this table shows that the elements examined require the same amount of heat from the beginning of the evaporation till gravity is overcome—as is required to overcome atmospheric pressure.

To sum up, Krafft maintains that boiling in the air depends on two factors, gravity and atmospheric pressure. By comparing vacuum boiling-points and air boiling-points he has a measure of atmospheric pressure. He believes that the lowest evaporation-point is the temperature at which single molecules begin to escape from the heated substance and that the interval between the evaporation-point and the vacuum boiling-point is a measure of gravity.

If he is right, it follows that, *at the earth's surface, gravity and atmospheric pressure are equivalent.*

E. RENOUF.

The Triphenylmethyl Question.

The triphenylmethyl question has assumed such an important position in the literature of organic chemistry that it has seemed well to prepare a brief report upon our knowledge of the substance. The work of Gomberg is so well known that only a few of the more characteristic properties of triphenylmethyl will be described here, while the greater part of this report will deal with certain suggestions as to the structure of triphenylmethyl which have been presented recently.

Triphenylmethyl was first obtained by Gomberg, in 1900, by the action of zinc upon triphenylchloromethane. The substance was found to be remarkably sensitive to certain reagents. It unites with atmospheric oxygen to form a peroxide, absorbs halogens readily and, in every way, exhibits the characteristics of an unsaturated compound. Finally, the cryoscopic determinations of the molecular weight, first made by Gomberg, indicated the unsaturated formula of triphenylmethyl as the correct expression of the structure of the substance. Later, however, Gomberg repeated his molecular weight determinations and found that his second series of measurements pointed to the double formula.¹ Notwithstanding this fact, the formula of hexaphenylethane could not be ascribed to Gomberg's substance for the reason that Ullmann and Borsum² had obtained a hydrocarbon, by another method, to which they had given this formula. This substance, too, had previously been obtained by Gomberg,³ by a still different process. Since the so-called hexaphenylethane of Ullmann and Borsum was not identical with the triphenylmethyl of Gomberg, it became necessary to look elsewhere for an explanation of the phenomenon.

In a recent number of the *Berichte*,⁴ A. E. Tschitschibabin

¹ Ber. d. chem. Ges., **37**, 2037 (1904).

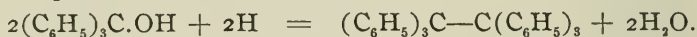
² *Ibid.*, **35**, 2877 (1902).

³ *Ibid.*, **35**, 3914 (1902).

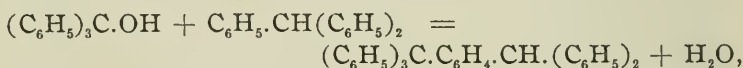
⁴ *Ibid.*, **37**, 4712 (1904).

points out that the hydrocarbon of Ullmann and Borsum is not hexaphenylethane, but an isomeric substance and that, in all probability, triphenylmethyl is the true hexaphenylethane. Tschitschibabin's argument is as follows :

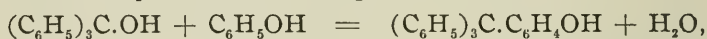
The hydrocarbon, obtained by Ullmann and Borsum and considered by them to be hexaphenylethane, was prepared by the action of zinc upon triphenylchlormethane in glacial acetic acid solution. In order to bring about a reaction, however, it was necessary to add zinc chloride. In their paper Ullmann and Borsum¹ express the belief that the reaction takes place in the following stages : Triphenylchlormethane is hydrolyzed by the small amount of water present in the acetic acid used and the triphenylcarbinol thus formed is reduced to hexaphenylethane by the hydrogen resulting from the action of the zinc upon the acetic acid :



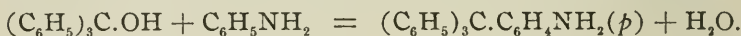
Since a condensing agent is necessary to bring about the reaction, Tschitschibabin thinks it probable that the condensation takes place in another manner and that pentaphenyldimethylbenzene (diphenylomethyltetraphenylmethane) is produced :



or that the condensation may take place between 2 molecules of the carbinol with a subsequent reduction to the above hydrocarbon. This reaction is made probable by the work of Baeyer and Villiger,² who showed that triphenylcarbinol condenses with phenol in an analogous manner :



and also by the work of Ullmann,³ who represented the condensation between triphenylcarbinol and anilin by the equation :



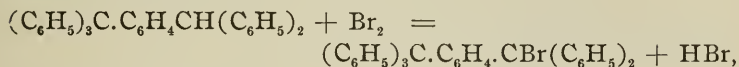
Ullmann and Borsum studied their substance carefully and came to the conclusion that its structure must be represented by the formula of hexaphenylethane. Tschitschibabin found, however, that, if dissolved in carbon bisulphide and placed in the sunlight, the hydrocarbon took up 1 atom of bromine and liberated hydrobromic acid. From this bromine derivative he was able to pass to the carbinol, acetyl and ethoxy compound. Finally, he proved that the bromine derivative is not a mixture

¹ Ber. d. chem. Ges., **35**, 2877 (1902).

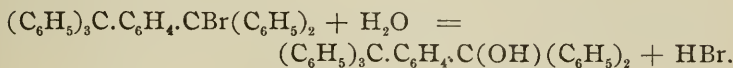
² *Ibid.*, **35**, 3018 (1902).

³ *Ibid.*, **36**, 404 (1903).

of substances containing bromine in a benzene nucleus. These reactions point, unmistakably, to the presence of a methane hydrogen atom and must be represented as follows :

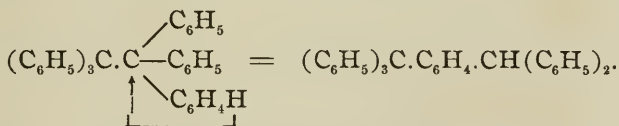


on treatment with water



From the results of these experiments Tschitschibabin suggests, as already mentioned, that triphenylmethyl is the true hexaphenylethane. He thinks that the marked reactivity of triphenylmethyl is not inconsistent with the structure of hexaphenylethane, because the presence of many electronegative groups tends to increase the activity of compounds. Peculiarities of structure often cause saturated compounds to act as though unsaturated ; *e. g.*, trimethylene passes readily into trimethylene bromide. Again, the work of Engler, Weger¹ and others has shown that many substances react with the oxygen of the air, at ordinary temperatures, to form peroxides as their first product. This phenomenon occurs with certain saturated compounds and is, probably, more common than is ordinarily supposed. Finally and most important, Gomberg has shown that triphenyliodomethane forms a peroxide with the same ease as triphenylmethyl itself.

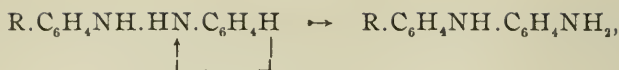
In the succeeding number of the *Berichte* an article by P. Jacobson appears,² in which he offers another suggestion. The fact, shown by Gomberg, that triphenylmethyl is converted, by hydrochloric acid, into the compound of Ullmann and Borsum, makes it seem improbable that triphenylmethyl is the true hexaphenylethane, especially when the structure assigned to the Ullmann and Borsum compound by Tschitschibabin is considered. If so, this rearrangement must take place in the following manner :



While analogy for such a transposition exists in the semidine rearrangement of the hydrazo bodies,

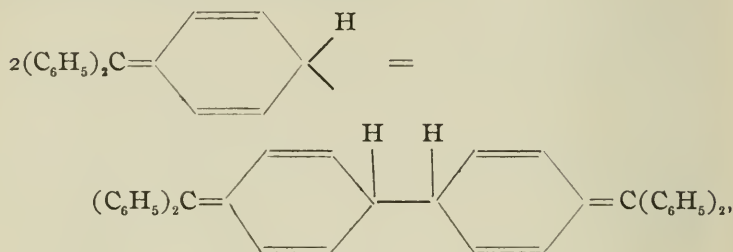
¹ Ber. d. chem. Ges., 36, 309 (1903).

² *Ibid.*, 38, 196 (1905).



it seems improbable that it should take place in this case.

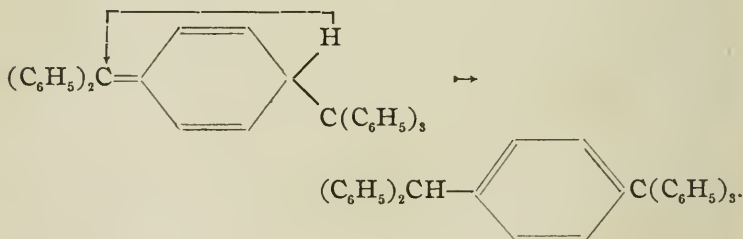
Jacobson's suggestion is founded upon the formula of a diquinoid proposed by Heintschel:¹



but with the difference that one quinoidal triphenylmethyl group is combined with one non-quinoidal triphenylmethyl complex, thus:

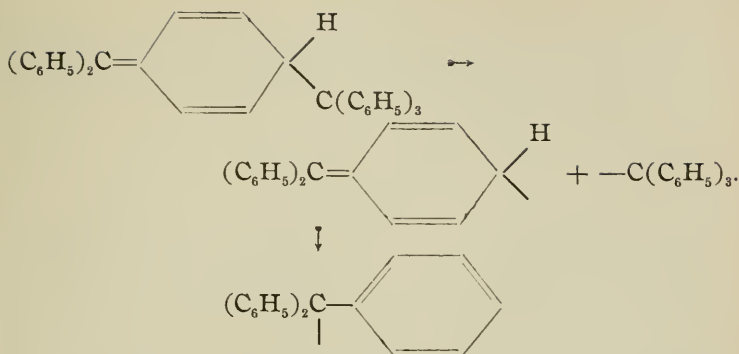


It has been shown by the work of Auwers, Bamberger, Zincke and others, that these quinoidal compounds exhibit a marked tendency to return to the aromatic condition. Should such a substance as the above rearrange, by the shifting of a hydrogen atom, the hydrocarbon of Ullmann and Borsum, as described by Tschitschibabin, would be formed:



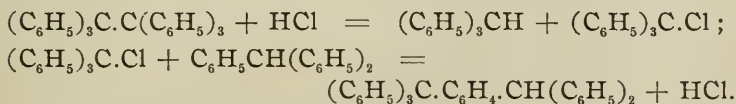
On the other hand, should the aromatic triphenylmethyl residue detach itself, a quinoidal triphenylmethyl would remain which could easily rearrange itself into the aromatic form by the shifting of its bonds:

¹ Ber. d. chem. Ges., 36, 320, 579 (1903).



Thus such a substance could readily react as triphenylmethyl and would be in accord with Gomberg's latest molecular weight determinations.

In a later number of the same journal¹ Tschitschibabin discusses the suggestion of Jacobson. He admits that the change of triphenylmethyl into the hydrocarbon of Ullmann and Borsum is easily explained by the quinoidal formula, but sees no special advantage in the monoquinoidal formula of Jacobson over the diquinoidal formula of Heintschel. Both quinoidal formulas seem improbable, however, when certain facts are considered. There undoubtedly exists a close relationship between triphenylmethyl and its haloid compounds. This is shown by the easy formation of triphenylmethyl by the action of metals; such as silver, on the haloid compounds. Since the work of Baeyer and Villiger makes it improbable that these haloid compounds have the quinoidal structure, it is hardly probable that triphenylmethyl possesses it. There seems to be no reason to doubt the capability of existence of such compounds as hexaphenylethane and, if Gomberg's hydrocarbon is indeed such, the change into the hydrocarbon of Ullmann and Borsum, by means of hydrochloric acid, can readily be explained by the assumption that the elements of hydrochloric acid are absorbed, with the formation of 1 molecule of triphenylmethane and 1 of triphenylchlormethane and that a condensation between these then occurs, with the liberation of hydrochloric acid:



The question is still an open one. Both Tschitschibabin

¹ Ber. d. chem. Ges., 38, 771 (1905).

and Jacobson's ideas are valuable, whether or not either of them has reached the truth. The next paper of Gomberg, in which he will doubtless consider these suggestions, will be awaited with interest.

P. H. COBB.

REVIEWS.

THE STUDY OF THE ATOM; OR THE FOUNDATIONS OF CHEMISTRY. By F. P. VENABLE, PH.D., D.SC., LL.D., University of North Carolina. Easton, Pa.: The Chemical Publishing Company. 1904. pp. 290.

In the words of the author, "The purpose of this work is to trace the atomic theory of chemistry from its earliest conception to the present day. This forms the foundation of all chemical theory and has been offered as the best explanation of the constitution of matter and of the universe. This theory has had a longer life than any other philosophical or scientific conception, and has to-day more nearly its ancient form. It has lived through bitter attack, dialectic strife, and even persecution, and can number its martyrs. It has called to its service the master minds of the world and the greatest ingenuity in experiment and logic. It is not to be presumed that such a conception can be dismissed in a few slighting sentences or overturned by one or two crude hypotheses."

In successive chapters the author takes up:

- I. Ancient views as to the nature of matter.
- II. From the Greek philosophers to Dalton.
- III. The atomic theory of chemistry.
- IV. The relative weights of the atoms.
- V. The periodic or natural system.
- VI. Affinity, the atomic binding force.
- VII. Valence.
- VIII. Molecules and the constitution of matter.

He clearly recognizes that the early atomic theories were of no value to chemistry. They were not chemical theories. The title of Chapter III. emphasizes this—"The atomic theory of chemistry," which is, of course, the theory of Dalton. An unusually clear account of the evolution of Dalton's views is given, use being made of the recent work of Roscoe and Hardin.

The author has not, to say the least, lost his head on the subject of ions. In speaking of the ionic theory he says (p. 215): "There are many difficulties in the way of this theory and in some respects it is not a satisfactory solution of the problems. It is still under discussion. Manifestly it is of very limited application whatever of truth there may be in it, since

it applies fully only to certain bodies dissolved in particular solvents and then only in very dilute solutions." It may be said that the fact that substances are not, as a rule, completely dissociated is not to be regarded as an objection to the theory. It seems highly probable that dissociation of some kind is a factor of importance in a large proportion of the reactions that take place between substances. The theory has no doubt been, and still is, a powerful incentive to valuable experimental work.

Nothing new is presented under the head of Valence, that ever puzzling subject. The hypothesis of Richards, and that of Venable, are given some space. The latter no doubt tends in the right direction, though somewhat vague.

In the last chapter, which deals with "Molecules and the Constitution of Matter," all the modern improvements including electrons and the ether of Mendeléeff are met with and any one reading this chapter will have a very fair idea of the views that are now under discussion. In fact the whole book is recommended to those interested in the theories of chemistry.

Some errors have been noted. On page 43 "Berthollet" is used three times for "Berthelot." On page 83 the title of Berthollet's book should be "Essai d'une Statique chimique." On page 84 "Stoichiometrie" should be "Stöchiometrie." On page 122 "Ampere" should be "Ampère." On page 199 the title of Berthollet's book is again wrong, being given as "Essai de statique chimique." These are, however, small matters, and can be easily corrected.

I. R.

AN ATTEMPT TOWARDS A CHEMICAL CONCEPTION OF THE ETHER. By PROFESSOR D. MENDELÉEFF. Translated from the Russian by GEORGE KAMENSKY, A.R.S.M., of the Imperial Mint, St. Petersburg. London, New York and Bombay: Longmans, Green & Co. 8vo. 1904. pp. 51. Price, 80 cents.

The author is of the opinion that the ether must be a definite chemical substance and must have weight. He says, "Although sceptical indifference is prone to discern only a working hypothesis in the conception of the ether, yet the earnest investigator, seeking the reality of truth and not the image of fantasy, is forced to ask himself what is the chemical nature of the ether." * * * "If the question were restricted to the ether which fills space and serves as a medium for the transmission of energy, it would in a way be possible to limit oneself to the supposition of mass without reference to its chemical relations and even to consider the ether as a primary matter, just as the mass of a planet may be conceived without regarding its chemical composition. But such an indifferent, in-

definite ether loses all sense of reality and awakens the misgivings of the earnest investigator, directly he realizes that it must permeate all substances."

The investigation into the chemical nature of the ether is based upon two propositions: "(1) That the ether is the lightest (in this respect ultimate) gas and is endowed with a high penetrating power, which signifies that its particles have, relatively to other gases, small weight and extremely high velocity, and (2) that the ether is a simple body (element) incapable of entering into combination or reaction with other elements or compounds, although capable of penetrating their substance, just as helium, argon, and their analogues are soluble in water and other liquids."

An extension of the periodic arrangement of the elements provides a place for an element x in the zero group, which includes helium, neon, argon, krypton, and xenon, and series 0 which precedes series 1. In series 1 the only known element included is hydrogen. The author now assigns an unknown element y to this series. This element is the second member of the zero group. The atomic weight of y is not greater than 0.4 and is probably less. "Such an analogue of helium may perhaps be found in coronium, whose spectrum, clearly visible in the solar corona above (that is, further from the sun than) that of hydrogen, is simple like that of helium, which seems to indicate that it belongs to a gas resembling helium, which was also predicted from its spectrum by Lockyer."

But y with an atomic weight 0.4 and a probable density of 0.2 "cannot possibly be ether, its density being too great. It wanders, perhaps for ages, in the regions of space, breaks from the shackles of the earth and again comes within its sphere, but still it cannot escape from the region of the sun's attraction, and there are many heavenly bodies of greater mass than the sun. But the atoms of ether must be of another kind; they must be capable of overcoming even the sun's attraction, of freely permeating all space, and of penetrating everything and everywhere. The element y , however, is necessary for us to be able to mentally realize the lightest and, therefore, swiftest element x , which I consider may be looked upon as the ether." It is evident that the atomic weight of x must be so small that the element will not be held in the atmosphere of any of the stars. By means of a few assumptions which seem justifiable and a few simple calculations the author reaches the conclusion that "*the particles and atoms of the lightest element x , capable of moving freely everywhere throughout the universe have an*

atomic weight nearly one-millionth that of hydrogen and travel with a velocity of about 2250 kilometers per second."

All chemists and physicists will find this pamphlet interesting and suggestive.

I. R.

GRUNDZÜGE DER CHEMISCHEN PFLANZENUNTERSUCHUNG. By DR. L. ROSENTHALER. Berlin: Julius Springer. 1904 Price, 2.40 M.

This little book of 124 pages is intended to help the beginner, who seeks to know the real composition of plants, to proceed in a systematic way with his investigation.

In the introduction the author calls attention to the fact that it cannot be expected, in a complex like a plant, to work with the accuracy and certainty which characterize the methods applied to inorganic mixtures and even the best quantitative processes give, finally, only approximate results. Often it is far easier to be sure of the absence of a group of substances than of their presence. For example, if, in a plant extract, the common reagents which precipitate alkaloids give no reaction we may know that alkaloids are absent, but if a precipitate is produced it may be due to other nitrogenous bodies. The needs of plant chemistry are greater than ever, more is demanded by the physiologist, the pharmacist and the pharmacologist and the importance of the subject is such as to cause the author to demand that a thorough and systematic study of it be made in the universities.

The general part of the book treats of the methods of preparing the material—powdering, percolating, extracting, etc.

The preliminary tests to determine the character of the constituents are next described. The process of Stas-Otto for the solution of the glucosides and bitter principles and the separations effected by lead acetate are described in sufficient detail.

The special part treats of the separation and determination of the alkaloids, glucosides, fats, and oils, waxes, lecithins, ethereal oils, resins, tannins, phlotophenes, organic acids, albuminoids and their decomposition-products, enzymes, toxalbumins, carbohydrates and related substances and inorganic compounds.

Of particular interest are the data relating to enzymes and toxalbumins because the older works on this subject do not discuss these points.

The manual cannot fail to be of use both to the student and the chemist, engaged either in analysis or research.

H. W. WILEY.

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ELEKTROLYTISCHE VERFAHREN ZUR HERSTELLUNG PARABOLISCHER SPIEGEL. VON SHERARD COWPER-COLES, London. Zur Deutsche übertragen von DR. EMIL ABEL. Mit 13 Figuren und 2 Tabellen im Text. Verlag von Wilhelm Knapp, Halle, a. S. 1904. pp. 17. Price, M 1.00.

This little monograph contains a clear and concise account of the processes involved in the preparation of parabolic mirrors.

H. C. J.

MONOGRAPHIEN ÜBER ANGEWANDTE ELEKTROCHEMIE. XV. Band. Künstlicher Graphit. VON FRANCIS A. J. FITZ-GERALD, Chemiker der International Graphite Co., Niagara Falls, N. Y. Ins Deutsche übertragen von DR. MAX HUTH, Chemiker der Siemens und Halske, A. G., Wien. Halle, a. S.: Wilhelm Knapp. 1904. Price, M. 3.

Reviews of several of these monographs have appeared in THIS JOURNAL ; this one is of interest to chemists.

Mr. Fitz-Gerald first gives a brief historical sketch of the work of Despretz, Berthelot and Moissan and next considers the different methods of making graphite. Castner's patent was based on the observation that carbon electrodes, connected with a dynamo and heated by passing a powerful current through them, are converted into denser carbon, of graphitic character, losing volatile material.

Girard and Street patented a furnace for making electrodes. Carbon electrodes are passed, longitudinally, through a heated space, in which they are brought into thorough contact with the arc, converting the carbon into graphite ; by shifting a magnetic field the arc is directed as desired, thus securing thorough contact and complete change to graphite. The patentees found that an electrode made of retort carbon and tar was not as completely changed to graphite as one containing 2 per cent of silica, or boric acid, or iron oxide.

Acheson's process developed from the observation that carborundum, at high temperatures, changed to graphite, silicon being volatilized, $\text{CSi} = \text{C} + \text{Si}$. The graphite thus formed is remarkably pure, containing only 0.03 per cent impurity. The yield, however, is small ; the theoretical yield would be only 30 per cent of the original material ; in practice much less is obtained.

Acheson's theory is that the carbon of an impure coal unites at a high temperature with silicon, or other elements, forming pure carbides, which, at higher temperatures, dissociate into pure graphite and the other element or elements, which are volatilized. He uses either silica, alumina, clay, lime, or iron oxide in forming such carbides.

Most of the artificial graphite marketed is made from anthracite. In the patent for this process Acheson enlarges his

theory. He says that it is not necessary to add the amount of silica, or other foreign substance, required to combine with all of the carbon to form a carbide, but that a small amount of such substance can decompose large quantities of carbon, yielding graphite, the process being the formation and decomposition of carbide, into graphite and the foreign element, which unites with the carbon from anthracite again, until the carbon is thus completely changed to graphite. He finds, also, that anthracite containing, as natural impurity, 5 per cent of silica, alumina and iron oxide gives better results than any artificial mixture of these substances with pure carbon.

In a brief supplement the author refers to recent work of himself and others on this subject. E. R.

LA STATIQUE CHIMIQUE, Basé sur les Deux Principes Fundamentaux de la Thermodynamique, par le LIEUTENANT-COLONEL E. ARIES, Ancien Elève de l'École Polytechnique. Librairie Scientifique. Paris: A. Hermann. 1904. pp. 251. Price, 10 Fr.

This book on chemical statics, based on the two fundamental laws of thermodynamics, is clearly and concisely written and a useful addition to the literature of the field. An idea of the scope of the book can be obtained best by a glance at its contents. It treats of mixtures, the laws and equations of chemical equilibrium, the phase rule, some types of dissociation, solutions, separation of liquid mixtures, the mixed vapor emitted by a liquid mixture, a perfect gas, the law of Dalton and the principle of Gibbs, homogeneous systems, dilute solutions and osmosis.

The book would be more easily accessible and its value would be increased by a good subject and author index.

H. C. J.

APPLICATION OF SOME GENERAL REACTIONS TO INVESTIGATIONS IN ORGANIC CHEMISTRY. By DR. LASSAR-COHN, Professor of Organic Chemistry at the University of Königsberg. Authorized translation by J. BISHOP TINGLE, PH.D. (Munich), F.C.S., Johns Hopkins University. New York: J. Wiley & Sons; London: Chapman & Hall, Limited. 1904. pp. 101.

This valuable little book should be in the hands of every one engaged in research in the field of organic chemistry. The object of the author is stated by him thus: "The time has arrived when it is possible to formulate, for the conduct of some operations, a number of general rules derived from the enormous mass of experimental material which has accumulated, and, as a corollary, to develop considerably many methods which are in use for organic chemical investigations. It may be hoped that, in course of time, the blind, trial and failure

process may be increasingly restricted ; this little book is offered as an attempt to systematize methods of work and treats of the following topics : *Fixation of labile hydrogen atoms ; modification of reactions ; improvement in the conditions of reaction by due recognition of the circumstances in which the product is formed ; influence of neighboring atoms and atomic complexes ; also some remarks on the overstrain of reactions.*

Under the head of "influence of neighboring atoms and atomic complexes" the author says : " At present the number of definitely ascertained instances of protective action is somewhat limited ; reactions inhibited from this cause have usually failed to be recorded on account of their negative results. It is well known that certain acids are not esterified by means of a mixture of alcohols and sulphuric acid or hydrochloric acid, and that certain nitriles and amines are not hydrolyzed by the action of dilute acids."

The writer of this notice has been much interested in phenomena of the kind here referred to and, with a number of his students, has studied many such experimentally and the results have been recorded. Apparently the articles embodying these results are unknown to the author of the book.

The translation is smooth and readable.

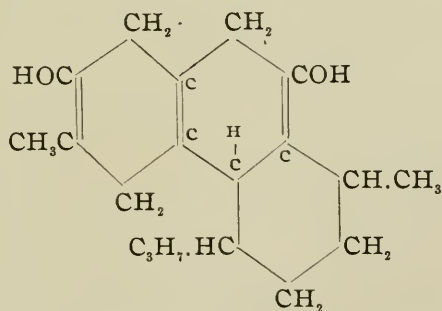
I. R.

AMERICAN CHEMICAL JOURNAL

CONTRIBUTION TO THE QUESTION OF THE CONSTITUTION OF ABIETIC ACID.

BY H. ENDEMANN.

The relation between abietic acid and reten was first considered by Tschirch and Studer,¹ who presented the following formula :



According to this, abietic acid should contain 2 hydroxyl groups and not 1 carboxyl group, as was formerly believed to be the case. The position of the methyl groups is, confessedly, arbitrary. However, the chief object of the two workers was

¹ Centrbl., 1903, ii, 1179.

to call attention to the relationship between reten and abietic acid; they did not offer any experimental facts but pointed out that the fossil resin reten is found in the soil of ancient pine forests.

A. Vesterberg¹ went one step further and prepared reten from abietic acid, by distillation with sulphur.

Both results point, therefore, to a relation between abietic acid and reten or another phenanthrene derivative, but it is, at present, by no means certain, even in the light of my own results, whether the third ring of the phenanthrene nucleus is originally present or whether it has not been formed from two aliphatic chains during the long period of time required for the production of reten in the soil, or even during the violent reaction with the sulphur in the retort. For the present I will formulate my results in accordance with the current views.

Abietic Acid Contains One Carboxyl Group.

Abietic acid heated at 160°, in a sealed tube, with excess of acetic anhydride, produces an oil, which can be freed from acetic acid and anhydride by protracted treatment with water, in which the oil is insoluble.

This oil is then saponified by alcoholic potassium hydroxide and the resulting product distilled with phosphoric acid and steam, in the apparatus previously described by me,² to recover the combined acetic acid.

Under the conditions of the experiment abietic acid is slightly volatile and it became necessary, therefore, to determine the acid value of this portion, which was accomplished by several blank experiments. Deducting the value so obtained, it was found that 1 gram of abietic acid combined with acetyl sufficient to form 0.207 gram of acetic acid, *i. e.*, for 1 molecule of abietic acid 1 molecule of acetic acid was obtained.

This points conclusively, therefore, to the assumption that abietic acid is really an acid and does not contain 2 hydroxyl groups as Tschirch and Studer state.

¹ Ber. d. chem. Ges., 36, 4200 (1903).

² Industrial Record, 1875. American Chemist, February, 1876.

Oxidation of Abietic Acid by Permanganic Acid in Acid Solution.

Abietic acid has been treated with oxidizing agents before, but usually the result has been a more or less far-reaching decomposition. Thus it is stated that abietic acid yields, with potassium permanganate, carbon dioxide, formic and acetic acids, while with chromic acid the product is chiefly acetic acid with some trimellitic acid.

Potassium permanganate, in strongly alkaline solution, acts less vigorously, so that by this means Mach obtained an acid with the formula $C_{10}H_{16}O_3$, which also indicates an extensive resolution of the original molecule.

Working in an acid solution, it was ascertained that, under certain conditions, products of definite composition could be obtained with less decomposition of the original compound. Ten parts of abietic acid are converted into the sodium salt, by heating with the requisite quantity of sodium hydroxide solution.

Fifteen parts of potassium permanganate are dissolved in so much water that, on cooling with ice, the salt remains in solution; an equivalent amount of sulphuric acid is then added.

The abietic acid solution is diluted to approximately the same volume as the permanganate solution, the two are thoroughly cooled with ice and then quickly mixed. The mixture at first becomes quite thick, owing to the separation of abietic acid, but it speedily becomes more mobile and manganese peroxide separates.

The quantity of ice in this solution should be ample to keep the mixture cold for some time, for heat is evolved during the reaction. The mixture is allowed to stand until the permanganic acid is completely reduced.

Sodium carbonate or hydroxide is now added, in slight excess and the whole is heated to boiling. The insoluble manganese oxides are filtered and the solution is evaporated.

When sufficiently concentrated, acid causes the precipitation of a resinous mass. On concentrating the supernatant liquid more of this resin is obtained. During the evaporation the

solution emits an odor resembling that of the lower fatty acids.

The resinous precipitate has a very decidedly bitter taste and was found to consist of two acids, which may be separated by their own varying solubility and by that of their salts.

An incomplete separation may be made by treating the mass with benzene, which, if not in too large excess, will dissolve one constituent almost wholly, this has a very intensely bitter taste; the residue contains another acid less bitter than the first.

The more soluble compound is completely separated from the residue by boiling it with barium hydroxide, in excess, cooling and filtering. The filtrate is then concentrated on the water-bath; when the salt commences to separate on the surface, the liquid is allowed to cool, again filtered and finally evaporated to dryness. This yields the barium salt of the acid less soluble in benzene.

The same acid may also be obtained, practically free from the other, by extracting the resinous precipitate repeatedly with benzene, dissolving the residue in alkali, boiling to remove all benzene and then reprecipitating the free acid. This removal of benzene by boiling is necessary, because the acid, although very sparingly soluble in benzene, is itself a good solvent for the latter, which it retains tenaciously. This affinity for solvents is, perhaps, the reason why, from most media, I did not succeed in obtaining the acid in a crystalline state. It may, however, be obtained in small crystals by the slow evaporation of its aqueous solutions, the most favorable condition being, apparently, a low temperature. The crystals generally form arborescent masses.

Other solvents such as epichlorhydrin, certain esters, chloroform, carbon tetrachloride, or carbon disulphide, leave the acid in an amorphous state, probably for the reason given above. Prolonged heating, at temperatures much above the boiling-points of the solvents, was necessary in order to remove the last traces of them from the acid. Acetone leaves the pure acid microcrystalline. Strong alcohol cannot be used as a solvent because the acid ~~esterifies very readily~~, even at the ordinary

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is readily esterified

temperature. This is evident from the fact that an alcoholic solution requires less and less sodium hydroxide for neutralization the longer it is allowed to stand. Two hours, at the ordinary temperature, are sufficient to raise the apparent equivalent of the acid 50 per cent. An acetone solution, however, can be used for the purpose of determining the equivalent of the acid acidimetrically. The acid is insoluble in petroleum ether and may be precipitated from the solutions of such solvents as will mix with petroleum ether and be freed from the other solvents and unchanged abietic acid, by treating with petroleum ether, in a Soxhlet apparatus.

The second acid is also insoluble in petroleum ether, but both dissolve, to some extent, particularly if the petroleum ether contains resins in solution and also in the presence of terpenes, or fatty substances. After being precipitated and washed in a Soxhlet apparatus for a considerable time, by petroleum ether, the acid forms a non-caking, sandy mass.

The bases with which the acid was combined are removed only with difficulty. After drying in air it melts at 80° and loses $1\text{H}_2\text{O}$, after which it melts at 111° – 113° .

Analysis:

0.1673 gram substance gave 0.4189 gram CO_2 = 68.29 per cent carbon.

0.1673 gram substance gave 0.1275 gram H_2O = 8.54 per cent hydrogen.

This agrees quite well with an acid of the formula $\text{C}_{16}\text{H}_{24}\text{O}_4$. The specimen was not entirely free from ash.

The average composition, deduced from 6 analyses of subsequent preparations, was:

	Calculated for $\text{C}_{16}\text{H}_{24}\text{O}_4$.	Found.
C	68.57	68.59
H	8.64	8.56

This substance has, therefore, been produced from abietic acid by the elimination of the group C_3H_4 and the addition of O_2 . It is a dibasic acid, with the equivalent = 139 (theory 140) as determined by titration in acetone solution; this corresponds to the molecular weight 280, for the formula $\text{C}_{16}\text{H}_{24}\text{O}_4$.

It forms an oily *diacetyl* compound, which was examined for acetic acid.

In boiling alcoholic solution the acid gives a precipitate with lead acetate. The percentage of lead in these precipitates, even when they were made from the same preparation is, however, not constant, perhaps because the acid has a great affinity for alcohol and forms, in part, an ester acid, the lead salt of which may, therefore, be present in the neutral lead salt. The formula $C_{16}H_{22}O_4Pb$ required 42.68 per cent of lead. The values obtained were: 41.40, 39.04, 36.69 and 36.4.

The acid, separated from the lead by hydrogen sulphide, always contains much sulphur and this method can, therefore, not be recommended for purification.

The acid is freely soluble in baryta water, even in the ratio 1 molecule barium hydroxide : 2 molecules of the acid. If this solution is boiled, a precipitate is formed, but if it is allowed to evaporate spontaneously it dries to a gummy mass.

If excess of barium hydroxide is used, *i. e.*, more than 1 molecule : 1 molecule of the acid and the solution is boiled, no precipitate is formed even after the excess of barium hydroxide has been removed. On slow evaporation crystals of the salt separate. They appear, under the microscope, as short columns, aggregating to arborescent masses. This salt, after drying at 90° – 95° , lost $3H_2O$ at 105° . It contains 33.06 Ba (33.07 calculated).

The second acid formed is found in the benzene solution, together with some of the first acid. It contains 1 oxygen atom less than the latter, *i. e.*, it contains the aldehyde group CHO in the place of CO_2H . Using the proportions of abietic acid and permanganic acid given above, it is the predominant product. It speedily reduces alkaline solution of a silver salt and also gives the aldehyde reaction with Schiff's reagent. The barium salt is difficultly soluble and may be used for the purification of the acid. The lead salt is soluble in alcohol, if it is prepared in boiling alcoholic solution, as described above.

For final purification the free acid is dissolved in benzene, precipitated and finally washed with petroleum ether, in a Soxhlet apparatus. The acid is generally obtained in an

amorphous state, the reason being, probably, the same as in the case of the other acid. From acetone solution it is deposited as a crystalline mass. I have not been able to obtain crystalline salts of this acid and yet it is a chemical individual, for the analyses invariably show the uniformity of the material and fractional precipitations do not exhibit such discrepancies as would suggest a mixture.

The dicarboxylic acid first described is quite soluble in water, indeed the resinous acid, which is recovered by the evaporation of the solution from which the crude mixture of the resins had been precipitated, is almost all dicarboxylic acid.

The aldehyde acid is quite sparingly soluble in water and stands about midway between the dicarboxylic acid and abietic acid, which is not absolutely insoluble.

For analysis the acid was dried at 100° , even at this temperature anhydride seems to form, though to a very limited extent.

	Calculated for $C_{16}H_{24}O_8$.	I.	Found. II.
C	72.66	72.72	72.95
H	9.17	9.00	9.01

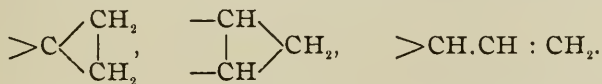
The acid, dried at 105° for several hours, gave :

	Calculated for anhydride.	Found.
C	75.36	74.11
H	9.11	9.15

The equivalent of the acid was ascertained by titration in acetone. Its melting-point is very easily affected by impurities. When highly purified it melts at 188° .

From the above results it follows that abietic acid contains a side chain C_4H_5 , constituted as $\cdot CH : C_3H_4$. Under the influence of an oxidizing agent the double bond is resolved and the CH becomes first CHO then CO_2H .

For the complex C_3H_4 three groupings are possible, viz. :



Recently, Tschirch and Studer have stated that they have been able, after much labor, to separate three abietic acids, α , β and γ , of which the last two have a tendency to pass into the α .¹

The most unstable would be :CH.CH : CH₂ and it could easily be understood how, under the influence of heat, it could condense into either of the other two, while it is less likely that these, when once formed, should change their constitution spontaneously.

However this may be, if there are three so nearly related I should think that commercial rosin contains all three groupings.

In order to verify still further the above results and conclusions, I have attempted to ascertain what had become of the group C₃H₄, which had been eliminated from the abietic acid. Starting with abietic acid, which had been prepared by saturating an alcoholic solution of rosin with hydrochloric acid and collecting the crystallized acid, I oxidized in the manner described above and used the mother-liquor from the precipitation of the crude acids. This was concentrated and the sulphates allowed to crystallize. The syrupy residue was then examined for a possible compound. After a series of unsuccessful experiments it was found that, when calcium chloride was added in excess and the calcium sulphate filtered off, a copious precipitate was formed by boiling the filtrate. This was thoroughly washed and, after drying, was found to contain 31.12 per cent calcium oxide. The calcium salt was suspended in water and oxalic acid added equivalent to the calcium found. The filtered liquid was then evaporated to dryness and the residue extracted with ether. On spontaneous evaporation, long needles of the acid were deposited.

From the percentage of calcium in the precipitate it was surmised that the acid thus formed was malonic acid. In order to verify this, it was converted into the diacetyl compound, which was heated, for some time, in a paraffin-bath, somewhat above 100°. The residue became yellow and dissolved in

¹ Centrabl., 1903, ii, 1178.

acetic acid, giving a yellow solution possessing the characteristic yellowish-green fluorescence. The acid is, therefore, ma-

lonic acid and is produced from the nucleus $\begin{array}{c} \text{—CH} \\ \text{—CH} \end{array} \rangle \text{CH}_2$ pres-

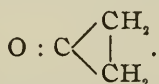
ent in the crystallizable acid and forming $\begin{array}{c} \text{CHO}_2 \\ \text{CHO}_2 \end{array} \rangle \text{CH}_2$.

Using commercial rosin, malonic acid is likewise formed, but in smaller quantity. If more permanganate is employed than above stated, the malonic acid may disappear entirely, which shows that malonic acid is destroyed by free permanganic acid.

A blank experiment with malonic acid showed it to be easily oxidized by free permanganic acid. The decomposition is accompanied by the evolution of carbon dioxide. The reaction was not followed further, but besides malonic acid there are formed :

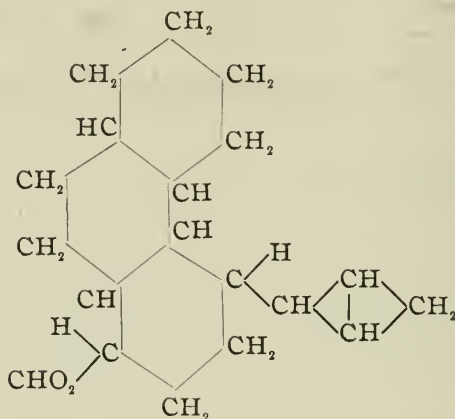
1. Syrupy acids.
2. An aromatically odoriferous, neutral substance. As yet, none of these have been identified.
3. A volatile acid, to the extent of about 2 per cent, which consists, in part, of acrylic acid. (Ready absorption of bromine with formation of a bromine addition-product, crystallizing in large hexagonal plates.) When known, these will lead eventually to the constitution of the isomeric acids, by determining the position of the atoms in the group C_3H_4 .

I consider it possible that the rosin in turpentine, as obtained in nature, contains the group :CH.CH:CH_2 , which would form acrylic acid and that the subsequent treatment, necessary for the production of commercial terpene and rosin, causes a condensation of this group into the one forming malonic acid, another one perhaps forming a ketone :



I am not prepared, as yet, to discuss these questions, but expect to do so later. Considering, now, the bearing of this in-

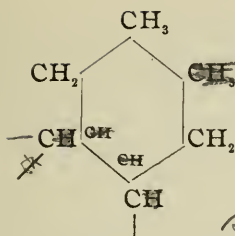
vestigation upon the formula of abietic acid and accepting the general opinion that abietic acid is a retene derivative, the formula must be written as follows :



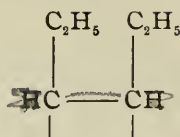
The positions which I have selected for these two side chains are such as to indicate the relation of the acid to retene and they agree with its formula, as determined by Bamberger and Hooker. The acid would be, therefore, a derivative of a fully hydrogenated phenanthrene, wherein 1 atom of hydrogen is replaced by the carboxyl group and 1 by the group C_4H_7 .

On this assumption the two resin acids formed would be tetradeca-hydrophenanthrenal carboxylic acid, $\text{C}_{16}\text{H}_{24}\text{O}_3$, and tetradeca-hydrophenanthrenedicarboxylic acid, $\text{C}_{16}\text{H}_{24}\text{O}_4$. Acids of the formula $\text{C}_{20}\text{H}_{30}\text{O}_2$ would, perhaps, have the side chain C_4H_7 and form propionic acid by oxidation. During the first stages of their production these acids are only partly in the free state. Another portion is in the form of a mixed anhydride, from which the free acids are produced by hydrolysis, whereby, on the one hand, the resinous acids described are formed and, on the other hand, malonic acid etc.

The possibility that abietic acid is, perhaps, not quite so closely related to phenanthrene and that all the rings given in the formula were not originally present, but that open chains, such as



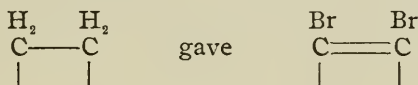
or

*see errata V. 34 p. 625*

were present, makes it necessary to consider the possible existence of a double bond between two of the carbon atoms.

Abietic acid is not very well adapted for the investigation of this point because a double bond exists in the side chain, but this is not the case with the dicarboxylic acid. This dibasic acid is dissolved in chloroform and excess of bromine added (3 : 2 by weight). After 2 days' standing in the cold, the hydrobromic acid which has been formed is shaken out with water and determined, while the acid in the chloroform is recovered by evaporation.

It was found that, for 2 atoms of bromine which had combined with the dicarboxylic acid, 4 molecules of hydrobromic acid had been formed. The reaction, therefore, was not only one of substitution but also one of condensation between two carbon atoms, now connected by a double bond :



This experiment is not absolutely convincing, but, so far, no facts have been brought out incompatible with the formula presented.

The many peculiarities in reactions and properties of the substances derived from rosin, must strike all those familiar with them, as presenting decided similarities and suggesting a close relationship to the bitter principles from hops. This is also observed in their action as preservatives, especially when the destruction of the organisms of acetic and lactic fermentations are concerned. Humulic acid and my dicarboxylic acid differ in composition by CH_4 , suggesting the presence of a pen-

tane ring with 1 double bond, already demonstrated,¹ in the place of a hexane ring. On this I shall report later.

In conclusion I wish to state that I have been very industriously helped in these investigations by my assistant, Mr. John W. Paisley, who deserves my sincere thanks.

Since writing the above I have noticed a paper by T. H. Easterfield and G. Bagley,² in which they also formulate abietic acid as a decahydrophenanthrene derivative, but with two double bonds, two of the hydrogen atoms being replaced by methyl and isopropyl. In all cases the assumption of the presence of these groups is based upon the reten formula, in which their presence has been recognized.

According to my investigation these groups are not originally present in abietic acid, but must be considered as being formed from the side chains, by the action of reducing agents and abietic acid itself must be considered as a tetradecahydrobutenylphenanthrenecarboxylic acid.

THE APPROXIMATE COMPOSITION OF THE HYDRATES FORMED BY CERTAIN ELECTROLYTES IN AQUEOUS SOLUTIONS AT DIFFERENT CONCENTRATIONS.

[TENTH COMMUNICATION.]

BY HARRY C. JONES AND H. P. BASSETT.

Nine papers³ have already been published by Jones and his co-workers in this laboratory, on the combination of solvent and dissolved substance in solution. In this, the tenth paper, the approximate composition of the hydrates, formed by a

¹ Lintner and Schnell: *Centrabl.*, 1904, i, 1227.

² *J. Chem. Soc.*, 85, 1238 (1904).

³ Jones and Chambers: *THIS JOURNAL*, 23, 189 (1900). Chambers and Frazer: *Ibid.*, 23, 512 (1900). Jones and Getman: *Ibid.*, 27, 433 (1902). Jones and Getman: *Z. physik. Chem.*, 46, 244 (1903); *Phys. Rev.*, 18, 146 (1904). Jones and Getman: *THIS JOURNAL*, 31, 303 (1904). Jones and Getman: *Z. physik. Chem.*, 49, 385 (1904). Jones and Getman: *Ber. d. chem. Ges.*, 37, 1511 (1904). Jones and Getman: *THIS JOURNAL*, 32, 308 (1904). Jones and Getman: *Ibid.*, 32, 308 (1904).

number of electrolytes in water, at different concentrations, is calculated.

In an earlier paper Jones and Getman¹ pointed out *a relation between the lowering of the freezing-point produced by electrolytes and their water of crystallization*. This relation was shown to hold for a large number of chlorides, bromides, iodides and nitrates. Indeed, for about 40 electrolytes with larger and smaller quantities of water of crystallization. The discovery of this relation confirmed us in the conclusion, reached much earlier by one of us,² that the abnormal freezing-point results produced by the electrolytes, especially in concentrated solutions, was due to a combination between the solvent and the substance dissolved in it.

Indeed, this conclusion seems to be almost a necessary consequence of the above relation. *If hydrates are present in such solutions, those substances that form the most complex hydrates in solution would be the substances that would crystallize from solution with the largest amounts of water*. This is the same as to say that those substances which, in solution, have the greatest power to combine with water, would be the ones that would bring with them the largest amounts of water out of solution.

We should, however, not expect the two phenomena to be exactly proportional to one another, because the actual shape of the molecules which build up the crystal would also be a conditioning factor in determining the exact number of molecules of water with which any given substance would crystallize.

The best we could hope to discover would be a general, qualitative relation between the lowering of the freezing-point and the water of crystallization. That such a relation actually exists can be seen by consulting Figs. I. to IV.

The data that are incorporated in these curves have already been published.³

In Fig. I., the results that have been obtained for the various chlorides, are plotted, as far as could be done on one sheet, without undue crowding. The abscissae are concentra-

¹ Z. physik. Chem., **49**, 385 (1904).

² Jones: THIS JOURNAL, **23**, 89 (1900).

³ *Ibid.*, **31**, 303 (1904). Z. physik. Chem., **46**, 244 (1903); **49**, 385 (1904).

tions expressed as gram-molecular normal, the ordinates are molecular lowerings of the freezing-point. The chlorides of

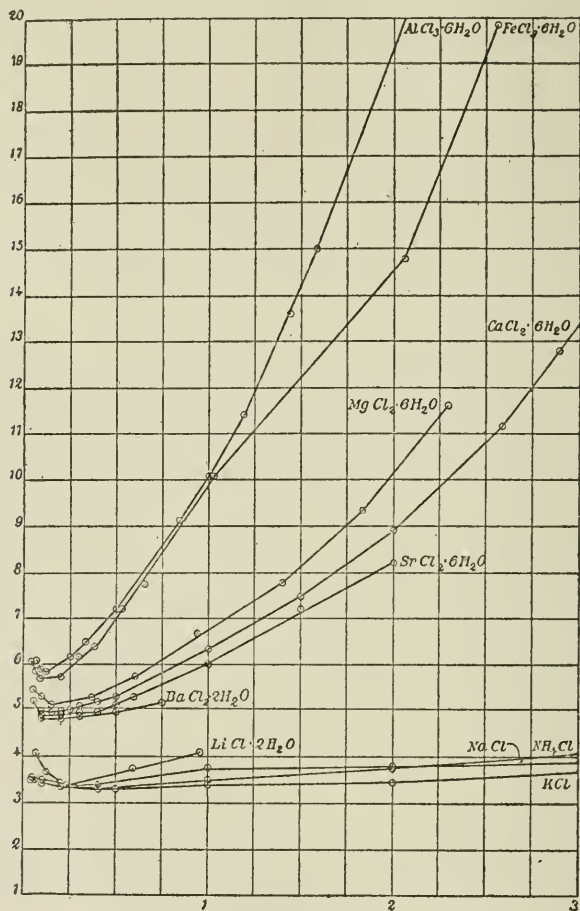


Fig. I.

sodium, potassium and ammonium, which crystallize without water, give the smallest lowering of the freezing-point.

The chloride of lithium, with 2 molecules of water of crystallization, gives considerably greater lowering of the freezing-point of water than the chlorides which have no water of crystallization.

When we pass to barium chloride, which contains 2 molecules of water of crystallization, it gives a greater lowering of the freezing-point than lithium chloride, with the same amount of water of crystallization. It must, however, be remembered in this connection that lithium chloride is a binary electrolyte, yielding only 2 ions, while barium chloride is a ternary electrolyte—each molecule dissociating into 3 ions.

Strontium, calcium and magnesium chlorides all crystallize with 6 molecules of water and all give freezing-point lowerings of the same order of magnitude.

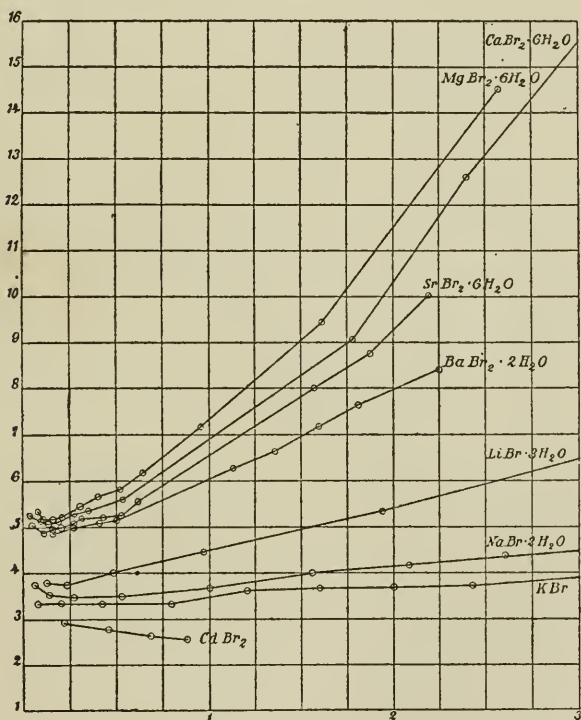


Fig. II.

Aluminium and ferric chlorides contain 6 molecules of crystal water, yet they show much greater lowering than the ternary chlorides with 6 molecules of water of crystallization. This is

to be accounted for by the fact that the chlorides of iron and aluminium are quarternary electrolytes—each molecule dissociating into 4 ions.

Turning to Fig. II., relations, similar to those pointed out above, are seen to exist for the bromides. Sodium bromide,

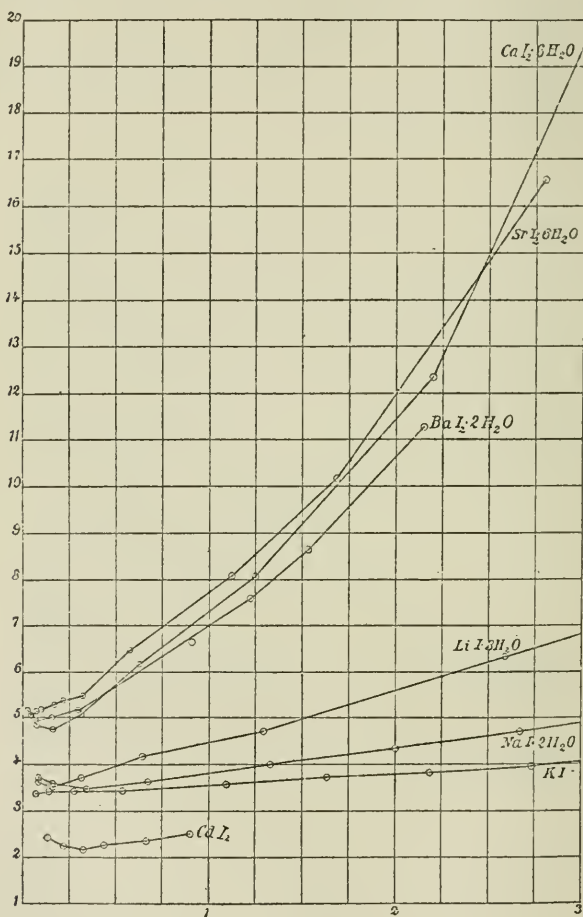


Fig. III.

unlike sodium⁷chloride, crystallizes with 2 molecules of water. It falls considerably above potassium bromide, just as we should

expect it to do. Lithium bromide, with 3 molecules of crystal water, occupies a still higher position in the figure. Passing to the ternary bromides, barium bromide, with 2 molecules of water of crystallization, shows greater lowering than the binary electrolyte, lithium bromide, as we should expect, it also gives considerably smaller lowering of the freezing-point than strontium, calcium and magnesium bromides, each with 6 molecules of water of crystallization.

Relations of an exactly similar character are shown by Fig. III., for the iodides.

The results plotted in Fig. IV., for the nitrates, present cer-

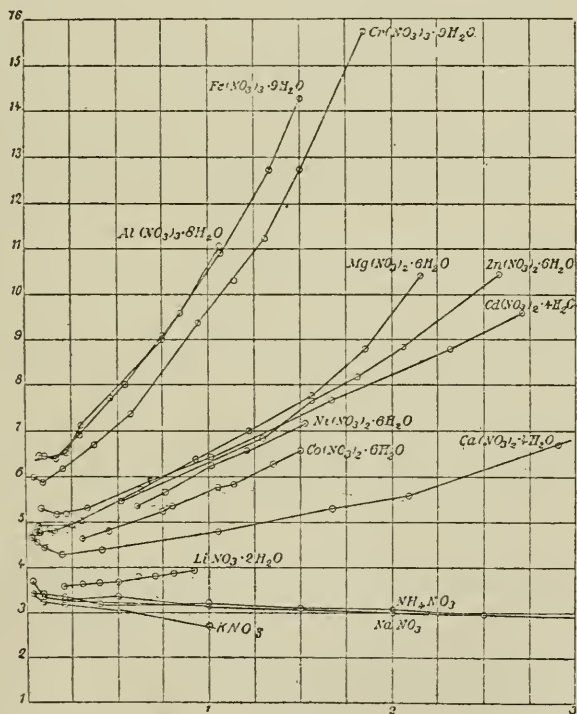


Fig. IV.

tain features of special interest. The nitrates without water of crystallization, sodium, ammonium and potassium, give the

smallest lowerings of the freezing-point. Lithium nitrate, with 2 molecules of crystal water, gives considerably greater lowering than the alkali nitrates.

Calcium nitrate crystallizes with 4 molecules of water and occupies a position in the figure about midway between the alkali nitrates without crystal water and a number of nitrates, each with 6 molecules of water of crystallization. Manganese nitrate, of all the nitrates studied, gives smaller lowerings than we should expect. We have repeated the experiments with this substance, to see if some error has not found its way into this part of the work.

The nitrates of a number of metals, each containing 6 molecules of water of crystallization, give lowerings of the freezing-point of the same order of magnitude and the curves for these substances fall very closely together on the figure.

The nitrates of aluminium, iron and chromium are of special interest, in that these substances contain more water of crystallization than any others thus far studied in this work. They not only show much greater lowering of the freezing-point than the nitrates with 6 molecules of crystal water, but show a greater lowering of the freezing-point of water than any other salts which we have thus far investigated. A careful study of this nitrate diagram, alone, will show an unmistakable relation between the lowering of the freezing-point and the water of crystallization possessed by the salts in question.

Relations such as those pointed out above, between *different salts of the same acid*, are all that could reasonably be expected to exist. Certain relations, however, of interest and importance in this connection, are found *between the salts of different acids*.

If we compare the results plotted in curves in Figs. I. to IV., for the chlorides, bromides, iodides and nitrates, we shall find abundant evidence bearing on the relation between freezing-point lowering and water of crystallization.

Take those chlorides, bromides, iodides and nitrates which crystallize without water; they all show a molecular lowering of between 3 and 4 and this increases very slightly, if at all, with the concentration.

As far as the comparison can be carried, lithium chloride, with 2 molecules of water, gives less lowering than lithium bromide or lithium iodide, with 3 molecules of water and just about the same lowering as lithium nitrate with 2 molecules of water of crystallization.

Lithium bromide, with 3 molecules of water, gives just about the same lowering as lithium iodide, which has the same amount of water of crystallization.

Sodium bromide, with 2 molecules of water, gives very nearly the same lowering as sodium iodide, which has the same number of molecules of water of crystallization.

Barium chloride has the same number of molecules of water of crystallization as the bromide and iodide. Since barium chloride has only a slight solubility in water, comparison of freezing-point lowerings must be limited to dilute solutions. The freezing-point lowerings of the three salts are just about the same in the dilute solutions, although in the more concentrated solutions the iodide shows greater lowering than the bromide.

If we compare the chlorides, bromides and iodides of the alkaline earths, which contain each 6 molecules of water of crystallization, we shall find that the lowerings of the freezing-point produced by them are all of the same order of magnitude. We shall, however, see that the bromides give somewhat greater lowering than the chlorides and the iodides even greater lowering than the bromides.

As far as comparisons can be made, it seems that the nitrates produce about the same lowerings as the corresponding chlorides with an equal number of molecules of water of crystallization and, therefore, somewhat less than the corresponding bromides and iodides.

The quarternary chlorides of aluminium and iron cannot be compared, at present, with respect to their freezing-point lowering, with the corresponding bromides and iodides, because the latter have not yet been investigated, but they will be studied as soon as possible.

A comparison of the lowerings produced by the chlorides of

iron and aluminium, containing 6 molecules of crystal water, with the nitrates of the same metals which have a larger amount of water of crystallization, will show a somewhat greater lowering, at the same concentrations, produced by the nitrates.

Thus, *relations between the lowering of the freezing-point of water produced by salts and their water of crystallization, comes out on every hand, whether we compare the salts of a given acid with different metals, or the salts of the same metal with different acids.*

This line of evidence, together with several others already pointed out in earlier papers, confirms us in the belief of the correctness of the theory, advanced by one of us,¹ to account for the abnormally great depressions of the freezing-point of water, produced by electrolytes, viz., *that in solution the dissolved substance is in combination with a part of the solvent; the amount of the solvent held in combination by the dissolved substance being a function of the concentration of the solution; in general, increasing with increase in concentration.*

In earlier papers² attempts were made to calculate the approximate composition of the hydrates formed by a number of substances at different dilutions. As was pointed out, this is not an easy matter for several reasons, especially on account of the difficulty of determining the dissociation in the more concentrated solutions. A number of the substances already studied undergo marked hydrolysis in dilute solution, so that it is impossible to determine the value of μ_{∞} in the usual way, by the conductivity method. A method, which would probably give μ_{∞} in such cases, that would not be very widely removed from the true value, was worked out and employed by Jones and Getman.³ It consists in combining the freezing-point and conductivity methods as follows: The dissociation for two or three dilute solutions of a substance was determined by the freezing-point method and their conductivities also measured. Knowing α and μ_v , μ_{∞} could be calculated at once. This method was proposed and applied, however, only tenta-

¹ Jones: THIS JOURNAL, 23, 89 (1900).

² Ibid., 31, 303 (1904). Z. physik. Chem., 49, 385 (1904).

³ THIS JOURNAL, 31, 303 (1904). Z. physik. Chem., 49, 385 (1904).

See previous
p. 647.

tively. It was pointed out that it is merely an approximation, but, with the data then at our disposal, it was the sole means of obtaining any idea as to the magnitude of the hydration for a given substance and of the change in the complexity of the hydrates with change in concentration.

It must also be repeated that the conductivity method is not an accurate measure of dissociation in concentrated solutions, yet it probably gives values of the right order of magnitude and, at present, is the best that can be done in such cases.

The Present Investigation.

The object of the present investigation is to calculate, as closely as possible, the composition of the hydrates formed by a number of electrolytes, over as wide range of concentration as work could be extended. In order to accomplish this the following data had to be secured: The lowering of the freezing-point, produced by the various solutions, had to be determined and the molecular lowering calculated from the observed value.

The conductivities of the solutions at 0° must be measured and also the value of μ_{∞} by the conductivity method, wherever this could be done. The object of these measurements was to ascertain, as closely as possible, the dissociation of the solution in question, in order that the theoretical lowering produced by the substance, if there was no hydration, could be calculated.

The specific gravities of all of the solutions must also be measured. The object of this was to determine the actual amount of water in a liter of the solution. The difference between the amount of water in a liter of a dilute solution and 1000 grams is small, but, in concentrated solutions, the difference may, of course, be very large.

Calculation of the Composition of the Hydrates.

Given the above data, the calculation of the amount of water in combination with the dissolved substance is simple. The observed molecular lowering is corrected for the difference between 1000 grams and the amount of water actually present

in 1 liter of the solution. This gives the true molecular lowering, produced by the substance at the dilution in question, if there were 1000 grams of water present.

The calculated molecular lowering can now be compared directly with the corrected, observed, molecular lowering. If there was no hydration these two values would be equal. The magnitude of the hydration is obtained as follows :

The calculated molecular lowering is divided by the corrected molecular lowering found. This ratio, multiplied by 1000, gives the amount of water present playing the rôle of solvent, if the quantity of the substance present was dissolved in 1000 grams of water.

The difference between this amount of water and 1000 grams is the quantity that is in combination with the dissolved substance, under the conditions that obtain in the solution in question.

For a number of reasons everything is referred to 1000 grams of the solvent. The theoretical freezing-point constant is calculated for 1000 grams of the solvent and, by calculating the depression found for the same amount of the solvent, the two sets of results are comparable. Further, by referring everything to a constant amount of the solvent, the various results can be compared directly with one another.

If we know the number of grams of water that have combined with the dissolved substance, the number of gram-molecules of water that have entered into combination is obtained by dividing the above value by 18. If we divide this value by the concentration in terms of normal, we obtain the number of molecules of water in combination with 1 molecule of the dissolved substance, when the amount of substance present in a liter of the solution is dissolved in 1000 grams of water.

The Results.

In order to calculate the composition of the hydrates formed by any given substance, at different dilutions, it is necessary to have the following values :

The lowering of the freezing-point produced by the dissolved substance.

The conductivity of the solution as an approximate measure of its dissociation.

The specific gravities of the solutions, in order to calculate the difference between 1000 grams of water and the amount contained in a liter of the solution.

Some of the above data were already available for the following substances. However, in many cases only a part of the data had been secured and this we have supplemented wherever necessary.

The compositions of the hydrates, formed by the following substances, are calculated as closely as seems to be possible, at present :

Calcium chloride, calcium bromide, strontium bromide, barium bromide, magnesium chloride and bromide, manganese chloride and nitrate, cobalt chloride and nitrate, nickel chloride and nitrate, copper chloride and nitrate and sulphuric acid.

In the various tables of data the symbols have the following significance :

In the tables of freezing-point measurements m is the concentration in terms of gram-molecules per liter ; Δ the observed freezing-point lowering, corrected for the separation of ice ; $\frac{\Delta}{m}$ the molecular lowering of the freezing-point.

In the conductivity tables the symbols have the usual significance, v is the volume of the solution, or the number of liters that contain a gram-molecular weight of the electrolyte, α is the approximate dissociation.

In the specific gravity tables m is the concentration, W_{Sol} is the weight of 25 cc. of the solution, W_{Salt} is the weight of the salt contained in 25 cc. of the solution, $W_{\text{H}_2\text{O}}$ is the weight of water contained in 25 cc. of the solution. The percentage correction is the correction that must be applied to the freezing-point lowering, in order to refer it to 1000 grams of solvent, instead of the amount of water that is present in a liter of the solution in question.

The symbols in the hydrate tables have the following significance : m is the concentration in terms of gram-molecules per liter, α the approximate dissociation of the solution, L the theoretical molecular lowering of the freezing-point referred to

1000 grams of the solvent, $\frac{\Delta}{m}$ the molecular lowering found experimentally, L' the molecular lowering, m' the number of gram-molecules of water in combination, both being referred to 1000 grams of water. H the number of molecules of water in combination with 1 molecule of the salt, at the concentration in question, if a liter of the solution, at that concentration, contained 1000 grams of water.

In order to ascertain the number of molecules of water actually in combination with 1 molecule of the dissolved substance, at the concentration given, it is only necessary to divide the value of M , for that concentration, by the concentration expressed in terms of a gram-molecular weight in 1000 grams of the solvent. The difference between the values of H found by these two methods is generally quite negligible, being smaller than experimental errors. It becomes appreciable only when the "correction" per cent is large, *i. e.*, in very concentrated solutions.

Calcium Chloride.

The data for calcium chloride are given in Tables I. to IV. The freezing-point lowerings had already¹ been determined and

Table I.—Freezing-point Measurements.

m .	Δ .	$\frac{\Delta}{m}$.
0.102	0°.505	4.98
0.153	0°.752	4.91
0.204	1°.012	4.96
0.255	1°.267	4.97
0.306	1°.537	5.02
0.408	2°.104	5.16
0.510	2°.681	5.26
0.612	3°.348	5.47
1.000	6°.345	6.345
1.500	11°.296	7.53 ¹
2.000	17°.867	8.934
1.949	17°.710	9.03
2.274	23°.000	10.11
2.598	29°.000	11.16
2.923	37°.400	12.79
3.248	46°.500	14.32

¹ Jones and Getman : Z. physik. Chem., 49, 442 (1904).

Table II.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 138.$$

v .	$\mu_v 0^{\circ}$.	α .
9.80	105.7	76.6
6.54	102.9	74.6
4.90	98.40	71.3
3.92	96.92	70.2
3.27	89.61	64.9
2.45	89.10	64.6
1.96	88.24	63.9
1.63	84.25	61.1
1.00	71.15	51.6
0.67	62.06	45.0
0.50	54.05	39.1
0.43	48.83	35.4
0.38	44.44	30.8
0.34	39.55	28.7
0.31	35.88	26.0

Table III.—Specific Gravity Measurements.

m .	W _{Sol} .	W _{Salt} .	W _{H₂O} .	Correction. Per cent.
0.102	25.2408	0.2831	24.9577	0.17
0.153	25.3166	0.4246	24.8920	0.43
0.204	25.4635	0.5661	24.8974	0.41
0.255	25.6176	0.7076	24.9100	0.36
0.306	25.7050	0.8492	24.8558	0.58
0.408	26.0032	1.1322	24.8710	0.52
0.510	26.2300	1.4152	24.8148	0.74
0.612	26.5403	1.6983	24.8420	0.63
1.000	27.3656	2.7750	24.5906	1.64
1.500	28.4996	4.1625	24.3371	2.65
2.000	29.5984	5.5500	24.0484	3.81
2.274	29.8363	6.2992	23.5371	5.85
2.598	30.4502	7.2150	23.2352	7.05
2.923	31.1440	8.0780	23.0660	7.74
3.248	31.7437	9.0188	22.7249	9.10

Table IV.—Hydrates.

<i>m.</i>	<i>α.</i>	<i>L.</i>	$\frac{\Delta}{m}$	<i>L'.</i>	<i>M.</i>	<i>H.</i>
0.102	0.766	4.71	4.98	4.97	3.02	29.6
0.153	0.746	4.64	4.91	4.89	2.84	18.6
0.204	0.713	4.51	4.96	4.94	4.84	23.7
0.255	0.702	4.47	4.97	4.95	5.39	21.2
0.306	0.649	4.27	5.02	4.99	8.02	26.2
0.408	0.646	4.26	5.16	5.13	9.42	23.1
0.510	0.639	4.24	5.26	5.22	10.41	20.4
0.612	0.611	4.13	5.47	5.44	14.40	23.5
1.000	0.516	3.78	6.345	6.24	22.80	22.8
1.500	0.450	3.55	7.53	7.33	28.65	19.1
2.000	0.391	3.31	8.934	8.59	34.15	17.1
2.274	0.354	3.08	10.11	9.52	37.58	16.5
2.598	0.308	3.01	11.16	10.37	39.43	15.2
2.923	0.287	2.93	12.79	11.80	41.76	14.2
3.248	0.260	2.83	14.32	13.02	42.81	13.2

a portion of the conductivity measurements made. The data necessary for calculating the hydration in dilute solutions was partly lacking and this was obtained.

The value of μ_{∞} for calcium chloride and for a number of the other salts used in this work, was determined by Mr. West, to whom we wish to express our thanks.

From column *m* it will be seen that the amount of water that has entered into combination increases with the concentration of the solution. This is just what we should expect from the law of mass action. The larger the amount of the salt present, the greater the amount of water that would be held in combination. The slight increase in the amount of water combined as we pass from 0.153 normal to 0.102 normal is to be noted, because a similar phenomenon occurs in other cases.

If we turn our attention to the number of molecules of water combined with 1 molecule of the dissolved substance, we shall see that this increases from the most concentrated solution to about half-normal and then, with considerable fluctuation, does not change in any decided manner. The number of molecules of water in combination with 1 molecule of the dissolved substance is really of less interest and importance than the *total amount* of water held in combination by the dissolved

substance, the latter has, therefore, been plotted in the curve (Fig. V.), against the concentrations as abscissae. The curve

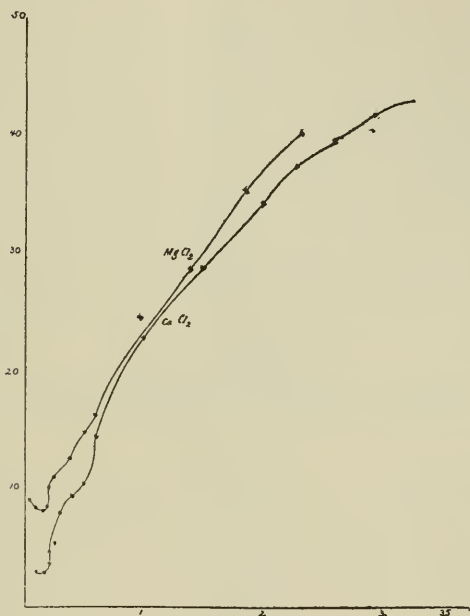


Fig. V.

shows, at a glance, that the amount of water held in combination increases, and fairly regularly, with the concentration.

Calcium Bromide.

What has been said in reference to calcium chloride holds largely for the bromide. Such data as were lacking were obtained, especially for dilute solutions, in order that the approximate magnitude of the hydration in such solutions could be calculated. The value of μ_∞ at 0° , for calcium bromide, was also obtained directly, by the conductivity method.

The total amount of water held in combination increases with the concentration (see Fig. VII., p. 558). The bromide combines with a little more water than the chloride, at the same concentrations.

Table V.—Freezing-point Measurements.

<i>m.</i>	Δ .	$\frac{\Delta}{m}$.
0.0435	0°.228	5.24
0.0871	0°.445	5.11
0.1306	0°.664	5.07
0.1742	0°.904	5.18
0.2613	1°.368	5.23
0.3484	1°.847	5.30
0.4355	2°.397	5.50
0.5226	2°.949	5.60
0.452	2°.340	5.18
0.903	6°.200	5.86
1.506	13°.100	8.69
1.807	17°.500	9.07
2.409	30°.500	12.66
3.011	47°.000	15.61

Table VI.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 123.7.$$

<i>v.</i>	$\mu_v 0^{\circ}$.	α .
22.98	107.42	86.8
11.48	100.53	81.3
7.66	98.29	79.5
5.74	94.53	76.4
3.83	93.19	75.3
2.87	89.44	72.3
2.30	87.59	70.8
1.91	85.86	69.4
1.11	80.9	65.4
0.66	68.3	55.2
0.55	61.7	49.9
0.415	50.14	40.5
0.332	39.68	32.1

Table VII.—Specific Gravity Measurements.

<i>m.</i>	W _{Sol.}	W _{Salt.}	W _{H₂O.}	Correction. Per cent.
0.0435	25.1605	0.2177	24.9428	0.23
0.0871	25.3421	0.4355	24.9066	0.37
0.1306	25.5154	0.6530	24.8624	0.55
0.1742	25.7263	0.8710	24.8553	0.58
0.2613	26.0433	1.3065	24.7368	1.05
0.3484	26.3743	1.7420	24.6323	1.47
0.4355	26.7319	2.1772	24.5547	1.78
0.5226	27.0749	2.6130	24.4619	2.15
0.9030	28.7128	4.5150	24.1978	3.21
1.5060	31.1185	7.5300	23.5885	5.65
1.8070	32.3080	9.0350	23.2730	6.91
2.4090	34.6443	12.0450	22.5993	9.60
3.0110	37.0233	15.0550	21.9683	12.13

Table VIII.—Hydrates.

m .	α .	L.	$\frac{\Delta}{m}$.	L'.	M.	H.
0.0435	0.868	5.13	5.24	5.23	1.06	24.4
0.0871	0.813	4.88	5.11	5.09	2.29	26.3
0.1306	0.795	4.82	5.07	5.04	2.43	18.5
0.1742	0.764	4.70	5.18	4.88	2.05	11.7
0.2613	0.753	4.66	5.23	5.18	5.58	21.3
0.3484	0.723	4.55	5.30	5.22	7.13	20.5
0.4355	0.708	4.49	5.50	5.40	9.36	21.3
0.5226	0.694	4.44	5.60	5.48	10.54	20.2
0.903	0.654	4.29	5.86	5.67	13.52	15.0
1.506	0.552	3.91	8.69	8.20	29.06	12.7
1.807	0.499	3.72	9.07	8.64	31.61	17.5
2.409	0.405	3.37	12.66	11.44	39.19	16.2
3.011	0.321	3.05	15.61	13.72	43.21	14.3

Strontium Bromide.

Although the freezing-point lowering had been determined¹

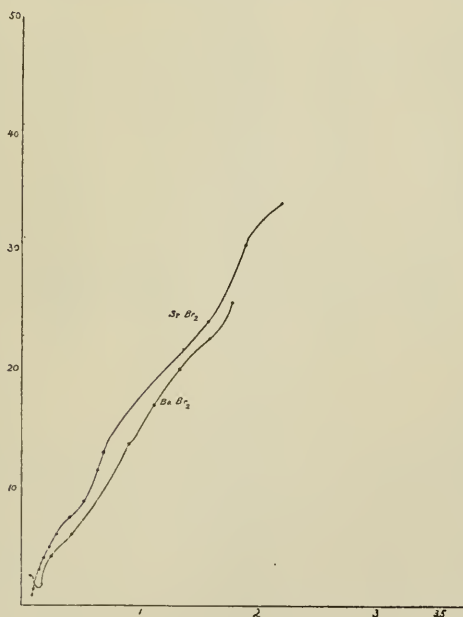


Fig. VI.

¹ Jones and Getman : Z. physik. Chem., 49, 405.

over the entire range of concentration that could be brought within this investigation, conductivity and specific gravity data had to be obtained. The value of μ_{∞} at 0° for strontium bromide was determined for us by Mr. West and is given below.

The results are of the same general character as those obtained with calcium chloride and bromide. The amount of water held in combination increases with the concentration, from the most dilute to the most concentrated solution and about the same quantity of water is combined as with the calcium salts, at the same concentration (see Fig. VIII., p. 563).

Table IX.—Freezing-point Measurements.

m .	Δ .	$\frac{\Delta}{m}$.
0.053	$0^{\circ}.262$	5.04
0.103	$0^{\circ}.503$	4.88
0.155	$0^{\circ}.773$	4.98
0.207	$1^{\circ}.035$	5.00
0.259	$1^{\circ}.308$	5.05
0.310	$1^{\circ}.592$	5.13
0.414	$2^{\circ}.147$	5.19
0.517	$2^{\circ}.741$	5.30
0.621	$3^{\circ}.447$	5.55
0.626	$3^{\circ}.502$	5.59
1.565	$12^{\circ}.520$	8.00
1.878	$16^{\circ}.500$	8.78
2.191	$22^{\circ}.000$	10.04

Table X.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 129.6.$$

v .	$\mu_v 0^{\circ}$.	α .
19.23	107.4	82.9
9.71	102.1	78.8
6.45	97.65	75.3
4.83	95.07	73.4
3.86	94.55	73.0
3.22	92.84	71.6
2.42	89.43	68.9
1.92	87.61	67.5
1.61	84.52	65.1
0.63	67.83	52.3
0.53	61.10	47.1
0.45	55.70	43.0

Table XI.—Specific Gravity Measurements.

<i>m.</i>	W _{Sol.}	W _{Salt.}	W _{H₂O.}	Correction. Per cent.
0.052	25.2438	0.3219	24.9219	0.31
0.103	25.5540	0.6376	24.9164	0.33
0.155	25.7882	0.9657	24.8225	0.71
0.207	26.0497	1.2872	24.7625	0.91
0.259	26.3649	1.6090	24.7559	0.98
0.310	26.6038	1.9201	24.6837	1.26
0.414	27.1646	2.5602	24.6044	1.58
0.517	27.6870	3.2002	24.4868	2.05
0.621	28.2420	3.8440	24.3980	2.40
0.626	28.1763	4.0734	24.1029	3.59
1.565	32.8955	9.7144	23.1811	7.28
1.878	34.4696	11.6325	22.8371	8.65
2.191	36.0403	13.5493	22.4910	10.04

Table XII.—Hydrates.

<i>m.</i>	α .	L.	$\frac{\Delta}{m}$.	L'.	M.	H.
0.052	0.829	4.94	5.04	5.02	0.886	17.0
0.103	0.788	4.73	4.88	4.86	1.488	14.4
0.155	0.753	4.66	4.98	4.94	3.15	20.3
0.207	0.734	4.59	5.00	4.95	4.04	19.5
0.259	0.730	4.57	5.05	5.00	4.78	18.4
0.310	0.716	4.52	5.13	5.07	6.04	19.5
0.414	0.689	4.42	5.19	5.11	7.50	18.1
0.517	0.675	4.37	5.30	5.19	8.78	17.0
0.621	0.651	4.28	5.55	5.42	11.69	18.8
1.565	0.523	3.81	8.00	6.70	23.96	15.3
1.8778	0.471	3.61	8.78	8.02	30.55	16.2
2.191	0.430	3.46	10.04	9.03	34.16	15.6

Barium Bromide.

The freezing-point measurements in the case of barium bromide had also been made,¹ but much of the other data had to be secured. We determined the value of μ_{∞} at 0° by the direct application of the conductivity method, at high dilutions.

The results obtained do not call for special discussion, because they are of the same general character as those already considered. The amount of the solvent held in combination

¹ Jones and Getman: Z. physik. Chem., 49, 407 (1904).

by barium bromide is about the same, at comparable concentrations, as for the other halides of the calcium group, after the first dilution, it increases with the concentration. The results are plotted in a curve, Fig. VI., p. 551.

Table XIII.—Freezing-point Measurements.

m .	Δ .	$\frac{\Delta}{m}$.
0.10	0°.506	5.06
0.15	0°.737	4.91
0.20	1°.001	5.00
0.40	2°.039	5.09
0.50	2°.591	5.18
0.4516	2°.310	5.11
0.6774	3°.890	5.74
0.9032	7°.300	5.87
1.1290	7°.050	6.24
1.3548	9°.020	6.66
1.5806	11°.260	7.12
1.8064	13°.860	7.67
2.258	19°.030	8.43

Table XIV.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 136.9.$$

v .	$\mu_v 0^{\circ}$.	α .
10.00	108.5	79.3
6.67	106.3	77.7
4.00	101.0	73.8
2.50	97.60	71.3
2.00	94.23	68.8
1.47	89.40	65.3
1.11	88.76	64.8
0.88	83.60	61.1
0.74	79.94	58.4
0.63	76.10	55.6
0.55	69.70	50.9
0.44	56.20	41.1

Table XV.—Specific Gravity Measurements.

<i>m.</i>	W _{Sol.}	W _{Salt.}	W _{H₂O.}	Correction. Per cent.
0.1	25.6280	0.7433	24.8847	0.46
0.15	25.9603	1.1149	24.8454	0.62
0.25	26.6335	1.8581	24.7754	0.90
0.40	27.5884	2.9730	24.6154	1.14
0.50	28.2854	3.7163	24.5691	1.72
0.6774	29.3522	5.0058	24.3464	2.61
0.9032	30.7874	6.6915	24.0959	3.62
1.1290	32.1553	8.4016	23.7537	4.99
1.3548	33.6259	10.0373	23.5886	5.65
1.5806	35.0292	11.7473	23.2819	6.87
1.8064	36.4501	13.4574	22.9927	8.03
2.258	39.2792	16.8031	22.4761	10.09

Table XVI.—Hydrates.

<i>m.</i>	α .	L.	$\frac{\Delta}{m}$.	L'.	M.	H.
0.10	0.793	4.81	5.06	5.04	2.54	25.4
0.15	0.777	4.75	4.91	4.88	1.48	9.9
0.25	0.738	4.60	5.00	4.96	4.03	16.1
0.40	0.713	4.52	5.09	5.03	5.63	14.1
0.50	0.688	4.42	5.18	5.09	6.22	12.5
0.6774	0.653	4.29	5.74	5.59	12.92	19.1
0.9032	0.648	4.27	5.87	5.66	13.64	15.1
1.1290	0.611	4.13	6.24	5.93	16.88	14.9
1.3548	0.584	4.03	6.66	6.28	19.90	14.7
1.5806	0.556	3.93	7.12	6.63	22.62	14.3
1.8064	0.509	3.75	7.67	7.06	26.05	14.4
2.258	0.411	3.39	8.43	7.58	30.71	13.6

Magnesium Chloride.

The freezing-point lowerings produced by magnesium chloride were measured by Jones and Getman.¹ The remaining data, especially for the dilute solutions, we have secured.

Magnesium chloride has greater power to combine with water than any of the halides of the calcium group. The difference is especially marked in the dilute solutions. Notwithstanding this fact, we see that the amount of water held in combination by the magnesium salt increases regularly with

¹ Z. physik. Chem., 49, 411 (1904).

increase in concentration (see Fig. V., p. 549). There is here also a slight exception presented by the first two solutions. It is worth noting that the amount of water combined with 1 molecule of the dissolved substances increases from the most dilute to the most concentrated solution.

Table XVII.—Freezing-point Measurements.

m .	Δ .	$\frac{\Delta}{m}$.
0.0508	0°.280	5.51
0.1016	0°.537	5.28
0.1525	0°.771	5.06
0.2033	1°.058	5.20
0.2541	1°.335	5.25
0.3801	2°.015	5.30
0.5082	2°.762	5.43
0.6099	3°.472	5.69
0.464	2°.482	5.35
0.927	6°.140	6.62
1.391	10°.820	7.78
1.854	17°.380	9.38
2.318	27°.000	11.60

Table XVIII.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 120.0.$$

v .	$\mu_v 0^{\circ}$.	α .
19.69	88.64	73.9
9.84	83.30	69.4
6.56	79.11	65.9
4.87	76.28	63.6
3.94	74.84	62.4
2.63	70.51	58.8
1.97	66.59	55.5
1.64	64.39	53.8
1.08	63.43	52.9
0.70	52.65	43.9
0.54	45.70	38.1
0.43	36.67	30.6

Table XIX.—Specific Gravity Measurements.

<i>m.</i>	W _{Sol.}	W _{Salt.}	W _{H₂O.}	Correction, Per cent.
0.0508	25.0818	0.1210	24.9608	0.16
0.1016	25.1641	0.2420	24.9221	0.31
0.1525	25.2596	0.3629	24.8967	0.41
0.2033	25.3275	0.4839	24.8436	0.62
0.2541	25.4230	0.6050	24.8180	0.73
0.3801	25.6426	0.9074	24.7352	1.06
0.5082	25.8768	1.2098	24.6670	1.33
0.6099	26.0392	1.4520	24.5872	1.65
0.927	26.7206	2.2134	24.5072	1.97
1.391	27.5109	3.3082	24.2027	3.19
1.854	28.3128	4.4030	23.9098	4.36
2.318	29.0447	5.5216	23.5231	5.91
2.782	29.8178	6.6164	23.2014	7.19

Table XX.—Hydrates.

<i>m.</i>	α .	L.	$\frac{\Delta}{m}$.	L'.	M.	H.
0.1016	0.694	4.44	5.28	5.26	8.41	82.7
0.1525	0.659	4.31	5.06	5.04	8.05	52.1
0.2033	0.636	4.23	5.20	5.17	10.10	49.7
0.2541	0.624	4.18	5.25	5.21	10.99	43.3
0.3801	0.588	4.05	5.30	5.24	12.62	33.2
0.5082	0.555	3.92	5.43	5.36	14.93	29.4
0.6099	0.538	3.86	5.69	5.60	17.26	28.3
0.927	0.529	3.83	6.62	6.50	23.93	25.8
1.391	0.439	3.49	7.78	7.53	29.81	21.4
1.854	0.381	3.28	9.38	8.97	35.29	19.0
2.318	0.306	3.00	11.60	10.91	40.28	17.4

Magnesium Bromide.

The bromide of magnesium, like the chloride, had already been studied by Jones and Getman.¹ They were interested especially in the magnitude of the hydration in concentrated solutions; much of the data necessary to calculate the approxi-

¹ Z. physik. Chem., 49, 412 (1904).

mate composition of the hydrates, in dilute solution, we had to secure.

The results for magnesium bromide are very similar to those for magnesium chloride. The amount of water held in combination is larger than in the case of any bromide of the calcium group. We notice here, also, a decrease in the value of m for the first two solutions, then a regular increase with the concentration (see Fig. VII.).

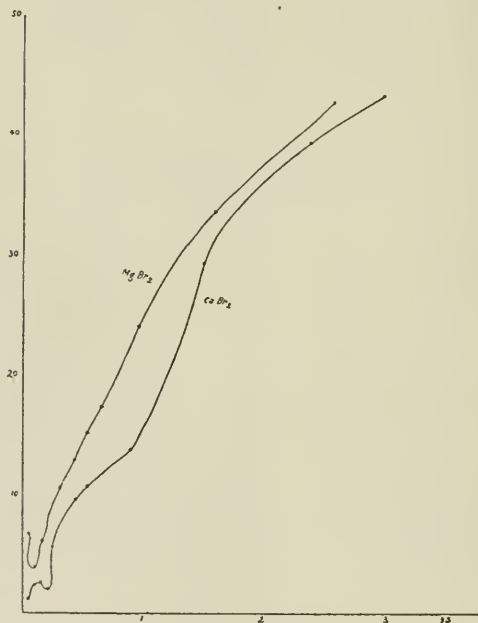


Fig. VII.

Here, again, the number of molecules of water combined with 1 molecule of the salt, increases from the most dilute to the most concentrated solution.

Table XXI.—Freezing-point Measurements.

m .	Δ .	$\frac{\Delta}{m}$.
0.0517	0°.277	5.36
0.103	0°.531	5.14
0.155	0°.801	5.17
0.207	1°.088	5.26
0.310	1°.690	5.45
0.414	2°.347	5.67
0.517	3°.022	5.84
0.321	1°.691	5.27
0.642	3°.921	6.17
0.964	6°.850	7.11
1.610	15°.200	9.44
2.571	37°.500	14.60

Table XXII.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 122.8.$$

v .	$\mu_v 0^{\circ}$.	α .
19.23	100.3	81.7
9.71	94.55	77.0
6.45	90.62	73.8
4.83	88.49	72.6
3.22	82.66	67.3
3.11	81.86	66.7
2.42	79.90	65.1
1.92	77.04	62.7
1.56	75.36	61.5
1.03	68.31	55.6
0.62	54.63	44.5
0.39	37.28	30.4

Table XXIII.—*Specific Gravity Measurements.*

<i>m.</i>	W _{sol.}	W _{salt.}	W _{H₂O.}	Correction. Per cent.
0.0517	25.1526	0.2379	24.9147	0.34
0.103	25.3540	0.4758	24.8782	0.49
0.155	25.5990	0.7138	24.8852	0.46
0.207	25.7553	0.9518	24.8035	0.79
0.310	26.1085	1.4275	24.6810	1.27
0.321	26.1549	1.4736	24.6813	1.27
0.414	26.5794	1.9070	24.6724	1.74
0.517	26.9461	2.3792	24.5669	1.73
0.642	27.3491	2.9472	24.4019	2.39
0.964	28.4985	4.4208	24.0777	3.69
1.610	30.7930	7.3680	23.4250	6.30
2.571	34.1739	11.9730	22.2009	11.19
3.214	36.1581	14.7360	21.4221	14.31

Table XXIV.—*Hydrates.*

<i>m.</i>	α .	L.	$\frac{\Delta}{m}$.	L'.	M.	H.
0.103	0.770	4.75	5.14	5.11	3.81	38.0
0.155	0.738	4.60	5.17	5.15	5.93	38.3
0.207	0.726	4.56	5.26	5.22	7.02	33.9
0.310	0.673	4.36	5.45	5.38	10.53	33.97
0.414	0.651	4.28	5.67	5.57	12.87	31.1
0.517	0.627	4.19	5.84	5.74	15.00	29.0
0.642	0.615	4.15	6.17	6.02	17.26	26.9
0.964	0.556	3.93	7.11	6.85	23.68	25.6
1.610	0.445	3.52	9.44	8.85	33.46	20.8
2.571	0.304	2.99	14.60	12.97	42.80	16.6

Manganese Chloride.

The substances dealt with in the remainder of this paper were studied by Jones and Getman,¹ in their earlier work. At that time the evidence for the existence of hydrates in solution was not recognized as clearly as it is to-day and no effort was then made to calculate the composition of the hydrates formed by these compounds.

We have taken the earlier data as far as they bear on the problem in hand and have supplemented them, wherever neces-

¹ THIS JOURNAL, 31, 303 (1904).

sary, in order to calculate the approximate composition of the hydrates formed by these various substances, at different concentrations. This necessitated many new freezing-point determinations; in all cases new conductivity measurements at

Table XXV.—Freezing-point Measurements.

m .	Δ .	$\frac{\Delta}{m}$.
0.053	0°.255	4.81
0.106	0°.508	4.79
0.133	0°.639	4.80
0.266	1°.259	4.73
0.400	2°.004	5.01
0.532	2°.790	5.24
0.796	4°.247	5.34
0.902	4°.825	5.36
1.061	5°.965	5.62
1.500	11°.100	6.66
2.000	16°.500	8.25
2.500	24°.000	9.60
3.000	31°.000	10.33
3.500	40°.000	11.43
4.000	48°.500	12.13

Table XXVI.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 123.$$

v .	$\mu_v 0^{\circ}$.	α .
18.87	88.67	72.0
9.43	81.81	67.0
7.51	79.85	65.0
3.76	73.49	60.0
1.88	65.16	53.0
1.26	57.32	47.0
0.94	51.44	42.0
0.66	43.35	34.0
0.50	34.82	28.0
0.40	26.38	21.0
0.33	19.67	16.0
0.29	14.04	11.0
0.25	9.82	8.0

Table XXVII.—*Specific Gravity Determinations.*

<i>m.</i>	<i>W</i> _{Sol.}	<i>W</i> _{Salt.}	<i>W</i> _{H₂O.}	Correction. Per cent.
0.133	25.2679	0.4186	24.8593	0.56
0.266	25.6125	0.8372	24.7753	0.90
0.400	25.9469	1.2590	24.6879	1.25
0.532	26.2766	1.6745	24.6021	1.59
0.796	26.9452	2.5154	24.4298	2.28
0.902	27.1870	2.8390	24.3480	2.61
1.061	27.6633	3.3394	24.3239	2.70
1.500	28.7249	4.7213	24.0036	3.98
2.000	29.8916	6.2950	23.5966	5.62
2.500	31.0396	7.8688	23.1708	7.32
3.000	32.0541	9.4425	22.6116	9.55
3.500	33.2645	11.0138	22.2507	11.00
4.000	34.5927	12.5900	22.0027	11.99

Table XXVIII.—*Hydrates.*

<i>m.</i>	<i>α.</i>	<i>L.</i>	$\frac{\Delta}{m}$.	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.133	0.65	4.28	4.80	4.77	5.7	42.8
0.266	0.60	4.09	4.73	4.69	7.1	26.7
0.532	0.53	3.83	5.24	5.16	15.4	28.9
0.796	0.47	3.61	5.34	5.22	17.13	21.5
1.061	0.42	3.42	5.62	5.47	20.8	19.6
1.500	0.34	3.12	6.66	6.40	28.9	19.3
2.000	0.28	2.90	8.25	7.79	34.9	17.5
2.500	0.21	2.64	9.60	8.90	39.1	15.6
3.000	0.16	2.46	10.33	9.34	40.9	13.6
3.500	0.11	2.27	11.43	10.18	43.2	12.3
4.000	0.08	2.16	12.13	10.68	44.3	11.1

0° and the specific gravities of all of the solutions had to be ascertained.

An examination of Table XXVIII. will show that manganese chloride resembles the chlorides already studied, in that the power to combine with water is great and increases regularly, from the most dilute to the most concentrated solution. This is also shown by the curve for this substance in Fig. VIII.

The number of molecules of water combined with 1 molecule

of the salt increases from the most concentrated to the most dilute solution. We have already met with other substances

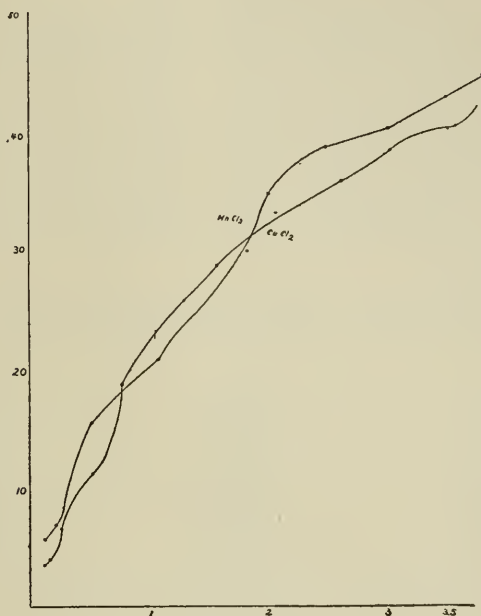


Fig. VIII.

where this is the case, notably magnesium chloride and bromide.

Manganese Nitrate.

The results formerly obtained by Jones and Getman¹ for manganese nitrate were somewhat out of keeping for a salt with 6 molecules of water of crystallization. The freezing-point lowerings, produced by this substance, were too small. Suspecting that there must have been some error, as far as this substance is concerned, we repeated the work. The following results were obtained :

From Table XXIX. it will be seen that manganese nitrate gives just about the same lowering of the freezing-point as other salts with 6 molecules of water of crystallization and

¹ THIS JOURNAL, 31, 313 (1904).

really falls right in line with the relation that has been shown to hold in such a large number of cases.

In order to avoid any possibility of error, we prepared a second, entirely new, solution of manganese nitrate and made a fresh standardization of this solution. The freezing-point lowerings, produced by solutions made from this newly standardized solution, were then determined, the results being recorded in Table XXXIII. It will be seen that these agree satisfactorily with the results in Table XXIX. The error in the original work with this substance was probably due to a mistake in standardization.

Table XXIX.—Freezing-point Measurements.

m .	Δ .	$\frac{\Delta}{m}$.
0.27	1°.39	5.15
0.54	2°.98	5.52
1.05	6°.75	6.43
1.59	12°.00	7.55
2.61	27°.50	10.54
3.15	38°.50	12.22

Table XXX.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 112.$$

v .	μv .	α .
3.70	80.62	72.0
1.85	71.37	63.7
0.95	58.48	52.2
0.63	48.61	43.4
0.38	27.37	24.4
0.32	20.02	17.9

Table XXXI.—Specific Gravity Measurements.

m .	W _{Sol} .	W _{Salt} .	W _{H₂O} .	Correction. Per cent.
0.27	25.8667	1.2087	24.6580	1.37
0.54	26.7980	2.4175	24.3805	2.48
1.05	28.4612	4.8350	23.6262	5.50
1.59	30.2003	7.1184	23.0819	7.67
2.61	33.4161	11.6850	21.7311	13.08
3.15	35.0516	14.1026	20.9490	16.20

Table XXXII.—Hydrates.

<i>m.</i>	<i>α.</i>	<i>L.</i>	$\frac{\Delta}{m}.$	<i>L'.</i>	<i>M.</i>	<i>H.</i>
0.09	0.824	4.93	5.11	5.09	1.75	19.4
0.18	0.766	4.71	4.90	4.86	1.72	9.53
0.27	0.720	4.54	5.15	5.08	5.91	21.87
0.54	0.637	4.23	5.52	5.38	11.87	21.99
1.05	0.522	3.80	6.43	6.08	20.83	19.84
1.59	0.434	3.47	7.55	6.97	27.90	17.55
2.61	0.244	2.77	10.54	10.04	40.23	15.41
3.15	0.179	2.53	12.22	10.24	41.82	13.28

Table XXXIII.—Freezing-point Measurements.

<i>m.</i>	$\Delta.$	$\frac{\Delta}{m}.$
0.09	0°.46	5.11
0.18	0°.88	4.90
0.27	1°.43	5.30
0.54	3°.07	5.69
1.05	6°.80	6.47
1.59	11°.80	7.42
2.61	27°.00	10.35
3.105	38°.00	12.24

Cobalt Chloride.

Only a very small number of the results for cobalt chloride had been obtained by Jones and Getman.¹ This applies also to the freezing-point lowerings, since only those produced by dilute solutions had been measured. The same holds for the conductivity measurements; all of the specific gravity determinations have been made by us.

The results are just what we should expect. Cobalt chloride crystallizes with 6 molecules of water and, like the other chlorides with this amount of crystal water, has large hydrating power. The amount of water combined with the salt increases, regularly, with the concentration of the solution, as is shown by the curve for this substance in Fig. IX.

¹ THIS JOURNAL, 31, 322 (1904).

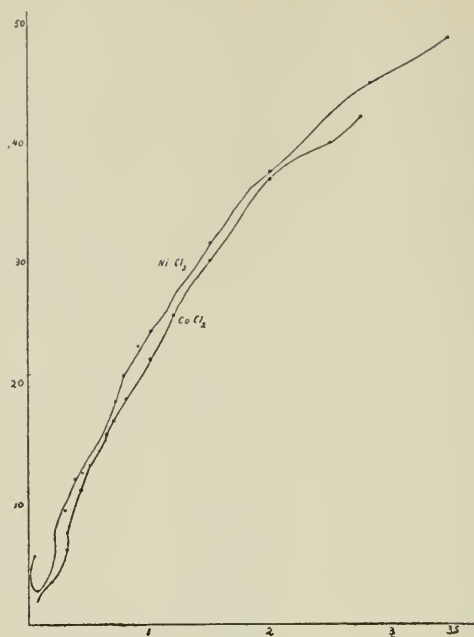


Fig. IX.

Table XXXIV.—Freezing-point Measurements.

m .	Δ .	$\frac{\Delta}{m}$.
0.0639	0°.325	5.09
0.1279	0°.631	4.94
0.1918	0°.946	4.93
0.3197	1°.640	5.13
0.4475	2°.427	5.43
0.5114	2°.817	5.51
0.6393	3°.658	5.72
0.700	4°.000	5.71
0.800	4°.700	5.88
0.900	5°.420	6.00
1.000	6°.240	6.24
1.500	11°.520	7.68
2.000	19°.000	8.50
2.500	27°.500	11.00
2.760	33°.500	12.14

Table XXXV.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 117.$$

$v.$	$\mu_v 0^{\circ}.$	$\alpha.$
15.65	95.93	82.0
7.82	88.42	75.6
5.21	86.36	73.9
3.12	79.50	67.9
2.23	74.45	63.6
1.95	71.53	61.1
1.57	67.94	58.1
1.43	64.38	55.0
1.25	61.48	52.6
1.11	58.93	50.3
1.00	57.25	48.9
0.667	47.34	40.5
0.50	37.93	32.4
0.40	29.79	25.5
0.362	26.13	22.3

Table XXXVI.—Specific Gravity Determinations.

$m.$	W _{Sol.}	W _{Salt.}	W _{H₂O.}	Correction. Per cent.
0.0693	25.1826	0.2077	24.9749	0.10
0.1279	25.3374	0.4154	24.9220	0.31
0.1918	25.5253	0.6229	24.9024	0.43
0.3197	25.8939	1.0382	24.8557	0.58
0.4475	26.2241	1.4533	24.7708	0.92
0.5114	26.4026	1.8583	24.5443	1.82
0.6393	26.7464	2.0761	24.6703	1.32
0.70	26.9935	2.2732	24.7203	1.12
0.80	27.2334	2.5980	24.6354	1.46
0.90	27.4400	2.9227	24.5173	1.93
1.00	27.7211	3.2475	24.4736	2.11
1.50	29.1942	4.8712	24.3230	2.71
2.00	30.4874	6.4950	23.9924	4.03
2.50	31.8077	8.1187	23.6890	5.24
2.76	32.5739	9.1931	23.3808	6.48

Table XXXVII.—Hydrates.

m .	α .	L.	$\frac{\Delta}{m}$.	L'.	M.	H.
0.0639	0.820	4.91	5.09	5.08	1.86	29.1
0.1279	0.756	4.67	4.94	4.92	2.71	21.2
0.1918	0.739	4.61	4.93	4.91	3.42	17.9
0.3197	0.679	4.39	5.13	5.10	7.73	21.1
0.4475	0.636	4.23	5.43	5.38	11.42	25.5
0.5114	0.611	4.13	5.51	5.41	13.14	25.7
0.6393	0.581	4.02	5.72	5.64	15.96	25.1
0.700	0.550	3.91	5.71	5.64	17.04	24.3
0.800	0.526	3.82	5.88	5.80	18.96	23.8
0.900	0.503	3.73	6.00	5.88	20.31	22.6
1.000	0.489	3.68	6.24	6.11	22.09	22.1
1.500	0.405	3.37	7.68	7.47	30.48	20.3
2.000	0.324	3.07	9.50	9.46	37.53	18.8
2.500	0.255	2.81	11.00	10.42	40.57	16.2
2.760	0.223	2.69	12.14	11.35	42.38	15.3

Cobalt Nitrate.

The nitrate of cobalt, like the chloride, crystallizes with 6 molecules of water of crystallization and we should expect hydrating power of the same order of magnitude. Such is the fact.

We worked with more concentrated solutions than had been previously used and supplemented the data obtained by Jones and Getman¹ for all of the solutions, so as to be able to calculate the composition of the hydrates at the various dilutions. The regular increase in the amount of water held in combination, with increase in the concentration of the solutions, is shown by the curve in Fig. X., p. 573.

Table XXXVIII.—Freezing-point Measurements.

m .	Δ .	$\frac{\Delta}{m}$.
0.0747	0°.352	4.72
0.1495	0°.685	4.58
0.2989	1°.388	4.65
0.4484	2°.198	4.87
0.7473	3°.935	5.28
1.0462	6°.025	5.76
1.3451	8°.418	6.26
1.4945	9°.811	6.55
2.000	17°.50	8.75
2.570	26°.50	10.60

¹ THIS JOURNAL, 31, 323 (1904).

Table XXXIX.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 117.6.$$

$v.$	$\mu_v 0^{\circ}.$	$\alpha.$
13.39	87.68	74.6
6.69	81.80	69.5
3.35	75.00	63.8
2.23	69.46	57.1
1.35	62.43	53.1
0.95	54.60	46.4
0.74	48.17	41.0
0.67	45.47	38.7
0.50	36.09	30.7
0.389	26.59	22.6

Table XL.—Specific Gravity Determinations.

$m.$	Wsol.	Wsalt.	WH ₂ O.	Correction. Per cent.
0.0748	25.2794	0.3422	24.9372	0.25
0.1495	25.5716	0.6843	24.8873	0.45
0.2989	26.0667	1.3931	24.6736	1.31
0.4484	26.6273	2.0523	24.5750	1.70
0.7473	27.6680	3.4204	24.2476	3.01
1.0451	28.7815	4.7834	23.9981	4.01
1.3451	29.7903	6.1565	23.6338	5.47
1.4945	30.2888	6.8403	23.4485	6.21
2.00	32.1172	9.1540	22.9632	8.15
2.57	33.9705	11.7629	22.2076	11.17

Table XLI.—Hydrates.

$m.$	$\alpha.$	$[\text{L}.$	$\frac{\Delta}{m}.$	$\text{L}'.$	$\text{M}.$	$\text{H}.$
0.0747	0.746	4.64	4.72	4.71	0.83	11.0
0.1495	0.695	4.45	4.58	4.56	1.34	9.0
0.2989	0.638	4.23	4.65	4.59	4.36	14.6
0.4484	0.571	3.98	4.87	4.79	9.39	20.95
0.7473	0.531	3.84	5.28	5.12	13.89	18.6
1.0462	0.464	3.59	5.76	5.53	19.49	18.6
1.3451	0.410	3.29	6.26	5.92	24.58	18.3
1.4945	0.387	3.10	6.55	6.14	27.51	18.4
2.000	0.307	3.00	8.75	8.04	37.31	18.6
2.570	0.226	2.70	10.60	9.42	39.63	15.4

Nickel Chloride.

The earlier work of Jones and Getman¹ had to do only with the more dilute solutions of nickel chloride. We have extended the earlier work from a concentration of only 0.743 N to 3.483 N.

The results with nickel nitrate are similar to those with cobalt chloride. The amount of water combined with the salt in solution increased regularly, from the most dilute to the most concentrated solution (see Fig. IX., p. 566). The number of molecules of water combined with 1 molecule of the salt increase, fairly regularly, from the most concentrated to the most dilute solution.

Table XLII.—Freezing-point Measurements.

<i>m.</i>	Δ .	$\frac{\Delta}{m}$.
0.037	0°.205	5.54
0.074	0°.380	5.11
0.149	0°.768	5.15
0.223	1°.170	5.25
0.297	1°.585	5.34
0.372	2°.032	5.46
0.446	2°.458	5.51
0.521	2°.945	5.65
0.743	4°.547	6.12
0.800	4°.880	6.10
0.900	5°.740	6.38
1.000	6°.580	6.58
1.500	11°.920	7.95
2.000	20°.000	10.00
2.500	31°.500	12.60
3.000	41°.500	16.60
3.483	53°.000	21.20

¹ THIS JOURNAL, 31, 317 (1904).

Table XLIII.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 120.7.$$

$v.$	$\mu_v 0^{\circ}.$	$\alpha.$
27.0	103.2	85.5
13.5	97.0	80.4
6.7	88.64	73.4
4.48	85.50	70.8
3.38	82.52	68.4
2.68	77.9	64.5
2.24	77.2	64.0
1.92	75.2	62.3
1.35	70.23	58.2
1.25	61.87	51.2
1.11	59.19	49.0
1.00	58.23	48.2
0.667	46.85	38.8
0.50	38.59	32.0
0.40	29.88	24.8
0.33	22.85	18.9
0.287	16.92	14.0

Table XLIV.—Specific Gravity Determinations.

$m.$	W _{Sol.}	W _{Salt.}	W _{H₂O.}	Correction. Per cent.
0.037	25.0835	0.1199	24.9636	0.15
0.074	25.1860	0.2398	24.9462	0.21
0.149	25.4198	0.4828	24.9370	0.25
0.223	25.6430	0.7225	24.9205	0.31
0.297	25.8450	0.9623	24.8827	0.47
0.372	26.0920	1.2028	24.8892	0.44
0.446	26.2954	1.4451	24.8503	0.60
0.521	26.4786	1.6881	24.7905	0.84
0.743	27.1588	2.4073	24.7515	0.95
0.800	27.3576	2.5920	24.7656	0.94
0.900	27.5953	2.9160	24.6793	1.28
1.000	27.9336	3.2400	24.6936	1.17
1.500	29.3731	4.8600	24.5131	1.55
2.000	30.7936	6.4800	24.3136	2.75
2.500	32.0714	8.1000	23.9714	4.11
3.000	33.5388	9.7200	23.8188	4.72
3.483	34.7943	11.2849	23.5094	5.96

Table XLV.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	$\frac{\Delta}{m}$.	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.074	0.804	4.85	5.11	5.10	2.73	36.9
0.149	0.734	4.60	5.15	5.14	5.83	39.2
0.223	0.708	4.49	5.25	5.23	7.86	35.2
0.297	0.684	4.40	5.34	5.31	9.41	31.7
0.372	0.645	4.26	5.46	5.43	11.97	32.2
0.446	0.640	4.24	5.51	5.48	12.57	28.2
0.521	0.623	4.16	5.65	5.60	14.28	27.4
0.743	0.582	4.04	6.12	6.06	18.52	24.9
0.800	0.512	3.76	6.10	6.04	20.97	26.2
0.900	0.490	3.68	6.38	6.31	23.15	25.7
1.00	0.482	3.65	6.58	6.50	24.36	24.4
1.500	0.388	3.30	7.95	7.83	32.14	21.4
2.00	0.320	3.05	10.00	9.73	38.08	19.0
2.500	0.248	2.78	12.60	12.18	42.88	17.2
3.00	0.189	2.56	16.60	15.82	46.57	15.6
3.483	0.140	2.38	21.20	19.85	48.90	13.8

Nickel Nitrate.

The freezing-point lowerings produced by solutions of nickel nitrate were studied pretty thoroughly by Jones and Getman. We have, however, been able to extend their investigations, even on freezing-point lowerings, to somewhat greater concentrations.

The hydrating power of nickel nitrate is of the same order as that of cobalt nitrate (see Fig. X., p. 573), just as we should expect, since it has the same number of molecules of water of crystallization.

Here, also, we notice that the number of molecules of water combined with 1 molecule of the salt, increases from the most concentrated to the most dilute solution.

¹ THIS JOURNAL, 31, 318 (1904).

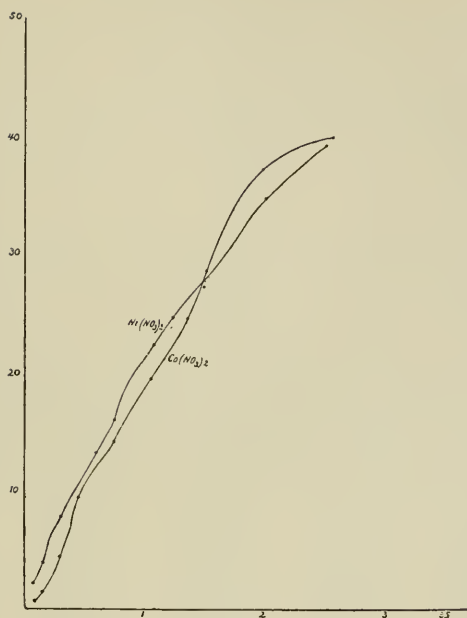


Fig. X.

Table XLVI.—Freezing-point Measurements.

m .	Δ .	$\frac{\Delta}{m}$.
0.0761	0°.377	4.95
0.1522	0°.750	4.93
0.3044	1°.527	5.01
0.6088	3°.273	5.37
0.7610	4°.306	5.66
1.0654	6°.691	6.28
1.2176	8°.006	6.58
1.5220	11°.883	7.15
2.000	17°.00	8.50
2.500	25°.00	10.00

Table XLVII.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 117.2.$$

$v.$	$\mu_v 0^{\circ}.$	$\alpha.$
13.13	90.90	77.5
6.57	85.14	72.6
3.25	76.00	64.8
1.64	68.60	58.5
1.31	61.90	52.8
0.90	55.30	47.2
0.82	52.28	44.6
0.65	45.29	38.6
0.50	34.25	29.2
0.40	26.11	22.3

Table XLVIII.—Specific Gravity Determinations.

$m.$	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.0761	25.2314	0.3477	24.8837	0.46
0.1522	25.5990	0.6955	24.9035	0.39
0.3044	26.1132	1.3910	24.7222	1.11
0.6088	27.2990	2.7819	24.5171	1.93
0.761	27.7974	3.4774	24.3200	2.72
1.0657	28.9284	4.8697	24.0587	3.76
1.2176	29.4458	5.5638	23.8820	4.47
1.522	30.6071	6.9548	23.6523	4.99
2.000	32.3305	9.1390	23.1915	7.23
2.500	34.0932	11.4237	22.6695	9.32
3.000	35.7096	13.7085	22.0011	12.00
3.394	36.9512	15.5093	21.4419	14.23

Table XLIX.—Hydrates.

$m.$	$\alpha.$	$L.$	$\frac{\Delta}{m}.$	$L'.$	$M.$	$H.$
0.0761	0.775	4.74	4.95	4.93	2.14	28.1
0.1522	0.726	4.56	4.93	4.91	3.96	26.0
0.3044	0.648	4.27	5.01	4.96	7.73	25.4
0.6088	0.585	4.04	5.37	5.27	12.97	21.3
0.7610	0.528	3.82	5.66	5.51	16.03	21.1
1.0654	0.472	3.61	6.28	6.04	22.35	22.0
1.2176	0.446	3.52	6.58	6.29	24.46	20.1
1.5220	0.386	3.30	7.15	6.79	28.55	18.8
2.000	0.292	2.95	8.50	7.89	34.71	17.4
2.500	0.223	2.69	10.00	9.07	39.08	15.6

Copper Chloride.

In the paper¹ to which reference has already been made, Jones and Getman attempted to calculate the approximate composition of the hydrates formed by copper chloride. In this calculation they had to make use of a part of the data obtained from other sources.

We have supplied this data for the various solutions, especially the specific gravities. We encountered difficulty in determining μ_{∞} for the copper salt. The value given was obtained by the conductivity method, taking into account the hydrolysis of copper chloride in dilute solutions.

The hydrating power of copper chloride is larger than would be expected from its water of crystallization. The increase in the amount of combined water, with the concentration, is seen in Table XLVIII. and in the curve in Fig. VIII., p. 563.

Table L.—Freezing-point Measurements.

<i>m.</i>	Δ .	$\frac{\Delta}{m}$.
0.065	0°.331	5.09
0.1301	0°.639	4.91
0.2602	1°.273	4.89
0.5204	2°.711	5.29
0.7806	4°.413	5.65
1.3010	8°.395	6.45
1.5612	10°.383	6.65
1.8210	12°.960	7.12
2.0816	15°.480	7.43
2.6020	20°.820	8.00
3.000	25°.50	8.50
3.500	31°.50	9.00
4.371	44°.50	10.19

¹ THIS JOURNAL, 31, 353 (1904).

Table LI.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 120.$$

$v.$	$\mu_v 0^{\circ}.$	$\alpha.$
15.30	94.42	78.7
7.64	88.06	73.4
3.84	78.38	65.3
1.92	67.68	56.4
1.28	59.30	49.4
0.76	48.22	40.2
0.64	39.32	32.8
0.55	35.02	29.2
0.48	30.81	25.7
0.38	22.58	18.8
0.33	17.48	14.6
0.29	13.05	10.9
0.23	7.61	6.11

Table LII.—Specific Gravity Measurements.

$m.$	W _{Sol.}	W _{Salt.}	W _{H₂O.}	Correction. Per cent.
0.0651	25.1985	0.2189	24.9796	0.08
0.1301	25.3934	0.4378	24.9556	0.18
0.2602	25.7941	0.8756	24.9185	0.33
0.5204	26.5913	1.7512	24.8401	0.64
0.7806	27.3458	2.6268	24.7190	1.12
1.3010	28.8280	4.3780	24.4500	2.20
1.5612	29.5841	5.2536	24.3305	2.68
1.8210	30.2350	6.1231	24.1119	3.55
2.0816	30.9999	7.0048	23.9951	4.02
2.6020	32.4090	8.7492	23.6598	5.36
3.000	33.3949	10.0875	23.3074	6.77
3.500	34.7877	11.8187	22.9690	8.01
4.371	36.9809	14.6975	22.2834	10.87

Table LIII.—Hydrates.

$m.$	$\alpha.$	L.	$\frac{\Delta}{m}.$	L'.	M.	H.
0.1301	0.734	4.59	4.91	4.90	3.53	27.1
0.2601	0.653	4.29	4.89	4.87	6.62	25.4
0.5204	0.564	3.96	5.29	5.26	13.73	26.4
0.7806	0.494	3.69	5.65	5.59	18.88	24.2
1.3010	0.402	3.36	6.45	6.31	25.97	20.0
1.5612	0.328	3.08	6.65	6.47	28.94	18.6
1.8210	0.292	2.95	7.12	6.87	30.03	16.5
2.0816	0.257	2.82	7.43	7.13	33.58	16.1
2.6020	0.188	2.66	8.00	7.57	36.03	13.9
3.000	0.146	2.40	8.50	7.92	38.72	12.9
3.500	0.109	2.27	9.00	8.28	40.33	11.5
4.371	0.064	2.10	10.17	9.77	49.77	11.4

Copper Nitrate.

What was said about the earlier work on copper chloride holds also, to some extent, for copper nitrate. Jones and Getman¹ calculated the approximate composition of the hydrates for a few solutions of copper nitrate. The data used were, however, partly taken from the work of others and interpolation was often necessary.

We have now obtained, with the same solutions, all the data necessary for calculating the composition of the hydrates. We encountered the same difficulty in determining μ_{∞} for copper nitrate as for copper chloride and solved the problem, approximately, in the same way. The hydrating power of copper nitrate is just about what we should expect it to be from its water of crystallization (see Table LII. and curve Fig. XI.).

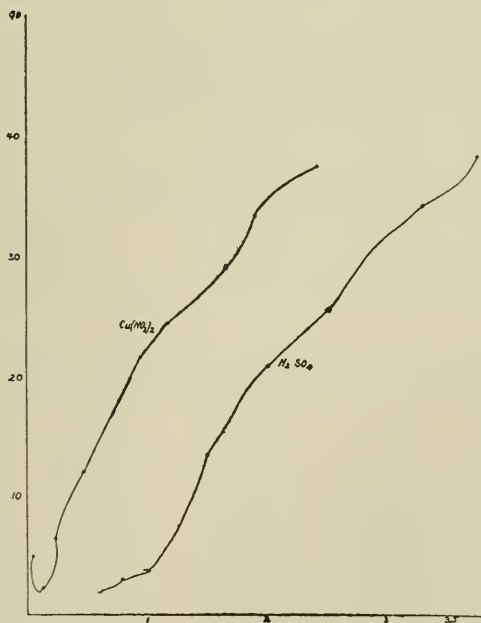


Fig. XI.

¹ THIS JOURNAL, 31, 353 (1904).

Table LIV.—Freezing-point Measurements.

m .	Δ .	$\frac{\Delta}{m}$.
0.0591	0°.326	5.52
0.1182	0°.595	5.03
0.2363	1°.210	5.12
0.4726	2°.544	5.39
0.9452	5°.903	6.26
1.1815	7°.799	6.60
1.6541	12°.650	7.07
1.8904	15°.490	8.20
2.3630	21°.890	9.26

Table LV.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 118.$$

v .	$\mu_v 0^{\circ}$.	α .
16.90	99.36	84.2
8.46	93.05	78.9
4.23	82.97	70.3
2.12	73.16	62.0
1.05	58.45	49.5
0.84	52.34	44.4
0.60	40.70	34.5
0.52	35.84	30.4
0.42	26.70	22.6

Table LVI.—Specific Gravity Determinations.

m .	W _{Sol} .	W _{Salt} .	W _{H₂O} .	Correction. Per cent.
0.0591	25.1456	0.2772	24.8684	0.53
0.1182	25.3851	0.5543	24.8308	0.68
0.2363	25.8364	1.1086	24.7278	1.09
0.4726	26.7265	2.2172	24.5093	1.56
0.9452	28.5284	4.4344	24.0940	3.62
1.1815	29.3289	5.5436	23.7853	4.86
1.6541	31.0048	7.7613	23.2435	7.03
1.8904	31.9184	8.8698	23.0486	7.80
2.363	33.6390	11.0872	22.5518	9.79

Table LVII.—Hydrates.

<i>m.</i>	α .	L.	$\frac{\Delta}{m}$.	L'.	M.	H.
0.1182	0.789	4.80	5.03	5.00	2.22	18.8
0.2363	0.703	4.48	5.12	5.07	6.47	27.4
0.4726	0.620	4.17	5.39	5.31	11.92	25.0
0.9452	0.495	3.70	6.26	6.03	21.47	22.7
1.1815	0.444	3.51	6.60	6.28	24.50	20.7
1.6541	0.345	3.14	7.07	6.55	28.92	17.5
1.8904	0.304	2.99	8.20	7.56	33.58	17.7
2.3630	0.226	2.70	9.26	8.35	37.59	15.9

Sulphuric Acid.

The approximate composition of the hydrates formed by sulphuric acid between the concentrations, normal and 4.37 normal, was calculated by Jones and Getman.¹

We desired to learn what order of hydration existed in both very concentrated and very dilute solutions of sulphuric acid. The freezing-points of its solutions were measured up to a concentration of 5N by means of an alcohol thermometer, using solid carbon dioxide and alcohol or ether as the refrigerating agents. The results are given in Table LVI. and in the curve (Fig. XI., p. 577).

In dilute solutions no water is held in combination. From about 0.5 to 5N the amount of combined water increases with the concentration.

Table LVIII.—Freezing-point Measurements.

<i>m.</i>	Δ .	$\frac{\Delta}{m}$.
0.10	0°.397	3.968
0.20	0°.670	3.850
0.30	1°.156	3.853
0.40	1°.570	3.920
0.60	2°.440	4.066
0.80	3°.300	4.125
1.00	4°.189	4.189
1.50	7°.443	4.962
2.00	11°.296	5.648
2.50	16°.275	6.510
2.73	21°.000	7.69
3.28	29°.000	8.84
3.825	41°.000	10.72
4.37	53°.000	12.13
4.50	58°.000	12.89
5.00	76°.000	15.20

¹ Z. physik. Chem., 49, 446 (1904).

Table LIX.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 500.$$

$v.$	$\mu_v 0^{\circ}.$	$\alpha.$
10.0	305.0	61.0
5.0	282.0	56.4
3.33	280.0	56.0
2.50	273.6	54.7
1.67	264.8	52.9
1.25	257.0	51.4
1.00	253.4	50.7
0.67	221.25	44.25
0.50	199.42	39.9
0.40	178.79	35.8
0.37	175.54	35.1
0.30	147.50	29.5
0.26	127.70	25.5
0.23	105.50	21.1
0.22	100.21	20.0
0.20	86.97	17.4

Table LX.—Specific Gravity Measurements.

$m.$	W _{Sol.}	W _{Salt.}	W _{H₂O.}	Correction. Per cent.
0.1	25.1307	0.2452	24.8855	0.46
0.2	25.2355	0.4904	24.7451	1.02
0.3	25.4205	0.7356	24.6849	1.26
0.4	25.5761	0.9808	24.5953	1.62
0.6	25.8572	1.4712	24.3860	2.46
0.8	26.1187	1.9616	24.1571	3.37
1.00	26.5028	2.4520	24.0508	3.80
1.50	27.2753	3.6780	23.5973	5.61
2.00	27.9968	4.9040	23.0928	7.63
2.50	28.7102	6.1300	22.5802	9.68
2.73	28.9777	6.6885	22.2892	10.84
3.28	29.8027	8.0360	21.7667	12.53
3.825	30.4816	9.3836	21.0980	15.61
4.37	31.1640	10.7065	20.4575	18.17
4.50	31.5062	11.0340	20.4722	18.11
5.0	31.9335	12.2600	19.6735	21.26

Table LXI.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	$\frac{\Delta}{m}$.	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.10	0.610	4.13	3.968	3.95		
0.20	0.564	3.96	3.850	3.81		
0.30	0.560	3.94	3.853	3.80		
0.40	0.547	3.89	3.920	3.86		
0.60	0.529	3.83	4.066	3.97	1.96	3.3
0.80	0.514	3.77	4.125	3.99	3.12	3.9
1.00	0.507	3.75	4.189	4.03	3.86	3.9
1.50	0.443	3.52	4.962	4.68	13.17	9.2
2.00	0.399	3.27	5.648	5.22	20.75	10.4
2.50	0.358	3.19	6.510	5.81	25.42	10.2
2.73	0.351	3.17	7.690	6.86	29.88	10.6
3.28	0.295	2.96	8.840	7.73	34.28	10.4
3.825	0.255	2.81	10.720	9.05	38.31	10.0
4.37	0.211	2.64	12.130	9.93	40.79	9.4
4.50	0.200	2.60	12.890	10.56	41.88	9.3
5.00	0.174	2.51	15.200	11.97	43.95	8.6

General Discussion of the Results.

It must be remembered that the problem of calculating even the approximate composition of the hydrates existing in solution is difficult. Some of these difficulties have already been mentioned. Certain assumptions must be made which are only approximately true. This is the case especially with the law of Raoult, which probably does not hold rigidly for concentrated solutions. Further, it has already been pointed out that the conductivity method is only a rough measure of the dissociation in concentrated solutions.

Taking all of the difficulties into account, we are still of the opinion that we can get a fairly good idea as to the composition of the hydrates, formed by the various electrolytes, in aqueous solutions of different concentrations.

An examination of the results recorded in this paper will show that the amount of water, held in combination by the dissolved substance, increases as the concentration of the solution increases. This is, of course, what would be expected in terms of mass action.

The number of molecules of water in combination with 1

molecule of the dissolved substance sometimes increases from the most concentrated to the most dilute solution, as with magnesium chloride and bromide, manganese chloride, nickel chloride and copper chloride.

With some substances the number of molecules of water held in combination by 1 molecule of the dissolved substance may pass through a well-defined maximum as the dilution is increased. In other cases, the number of molecules of water held in combination by 1 molecule of the dissolved substance may reach a maximum value as the dilution is increased ; this maximum value may then remain practically constant with further increase in the dilution. Examples of all of these conditions are to be found in the substances discussed in this paper. The probable explanation of these facts will appear in a subsequent communication.

An examination of the curves, Figs. V. to XI., will show that they are all of the same general type. These express the relation between the total amount of water in combination and the concentration of the solution. This resemblance in type is what we would expect, because the total amount of water held in combination by the dissolved substance is undoubtedly subject to the law of mass action.

Nature of the Compounds Formed.

The question arises whether these hydrates are true chemical compounds, as that term is ordinarily used, or whether they represent some less stable form of combination? That they are unstable is shown by the ease with which they are broken down by heat. Most of the water can be driven off, from the above solutions, at a temperature only a little above 100°. The more complex hydrates are, then, decomposed in solution at a comparatively low temperature and the water given off in the form of vapor. In the light of these facts the hydrates can scarcely be regarded as true chemical compounds. If, however, we insist on calling them chemical compounds, we must admit that they represent a very low order of stability.

A New Line of Evidence for the Theory.

The hydrates in solution are, as we have just seen, very unstable at the higher temperatures. *These hydrates become more and more stable the lower the temperature.* Hence, we might expect dissolved substances to be capable of bringing more and more water with them out of solution, the lower the temperature at which the crystals were formed.

An examination of the literature shows that this is the case. There is a comparatively large number of cases on record of salts crystallizing with different amounts of water; the lower the temperature at which the crystals were formed, the larger the number of molecules of water of crystallization.

This is exactly what we should expect from our theory of hydrates in aqueous solutions and from the increased stability of these hydrates as the temperature is lowered.

While the number of cases on record bearing on this point is large, we hope to be able to increase it in the near future. We shall make a systematic study of the problem in this laboratory, to see how greatly water of crystallization may be varied by crystallizing the salt at as widely different temperatures as possible.

Do Ions or Molecules Form Hydrates?

We are still of the same opinion as was expressed in the last communication¹ on this subject, that both the molecules and ions combine with water forming hydrates. It seems that the molecules are certainly capable of forming hydrates, because, in very concentrated solutions, where the molecules are present in large quantities, we often have considerable hydration and, further, Jones and Getman² have shown that certain non-electrolytes, such as glycerol, acetamide, fructose, etc., which are undissociated, still have the power of combining with water in solution, forming hydrates of even a high order of complexity.

That ions are capable of combining with water in solution, is shown by the magnitude of the hydration in many of the dilute solutions, where chiefly ions and only a few molecules are present.

¹ Jones and Getman : Z. physik. Chem., 49, 451 (1904).

² THIS JOURNAL, 32, 308 (1904).

Attention should be called to the fact that, in the preceding tables, the number of molecules of water in combination with 1 molecule of the dissolved substance is calculated for a molecule of the dissolved substance. If this molecule is dissociated into 2, 3, or 4 ions, the number given in column H in the tables would have to be divided by 2, 3, or 4, in order to ascertain how many molecules of water were in combination with an ion resulting from the dissociation of the molecule in question.

The Old and the New Hydrate Theory.

The theory of hydrates in aqueous solution that we believe to have established by the work, of which this is only a chapter, is to be sharply distinguished from the old hydrate theory of Mendeléeff, which, having long since been shown to be untenable, has been abandoned. According to the older theory, when a substance, like calcium chloride, is dissolved in water, there are formed certain definite chemical compounds, with perfectly definite amounts of water.

According to the theory established by this work, the compounds formed are, at best, very unstable and vary in combination all the way from 1 molecule of water to a very great number. The composition of the hydrate formed by any given substance is purely a function of the concentration of the solution, or is determined, as we say, by the effect of mass action. Thus, the composition of the hydrates formed by calcium chloride may vary all the way from a few molecules of water up to at least 30 molecules and may have all intermediate compositions, depending solely upon the concentration, temperature being, of course, understood to be constant.

It is thus obvious that the older and the newer hydrate theories are fundamentally different in character.

Summary.

1. Some of the evidence for the existence of hydrates in aqueous solutions of electrolytes has already been pointed out in earlier papers. The most direct and convincing evidence is to be found in the relation between the water of crystallization

and the magnitude of the freezing-point lowering. The plates of curves that bring out this relation, together with a brief discussion of the results, are given at the beginning of the present paper.

2. The chief object of this part of the investigation is to calculate, as closely as possible, the amount of water that is in combination with the dissolved substance at the various concentrations of the solutions. In the earlier preliminary calculations certain assumptions had to be made, for lack of sufficient data. This data we have now supplied, as far as possible, for 15 of the electrolytes with which we had already worked.

3. The amount of water held in combination by the dissolved substance increases with the concentration of the solution. That this increase is regular, to within the limits of experimental error, is shown by the curves, Figs. V. to XI.

4. The amount of water combined with 1 molecule of the dissolved substance, in some cases increases from the most concentrated to the most dilute solution. In other cases it passes through a maximum, in still others it acquires a maximum value, which remains practically constant with further increase in the dilution of the solution.

General Significance of the Results.

These results certainly have a direct bearing on the whole subject of solutions. They afford, at least, a partial explanation of the apparent failure of the gas laws to hold for concentrated solutions. Such solutions are obviously much more concentrated than we should suppose them to be from the amount of dissolved substance that is present in them. A part of the water present being in combination, there is just so much less water left in the solution to play the rôle of solvent and the solution is concentrated by just this amount. In the case of nearly every substance which crystallizes with a large amount of water, this change in concentration is large and, in many cases, of enormous magnitude.

Future Work.

We shall take up a much larger number of substances ; at first those for which data have been partially determined in earlier investigations in this laboratory and calculate, as closely as possible, the composition of the hydrates formed. We shall then bring within the scope of this investigation many new substances upon which we have not yet had time to work.

We propose also to study the effect of one substance, with large hydrating power, upon another with smaller power to form hydrates, when both are simultaneously present in the solution. Indeed, the number of problems that are opened up as the result of showing that combination between solvent and dissolved substance takes place, is almost unlimited.

We propose to extend this work much farther, to solvents other than water.

This investigation was carried out under a grant from the Carnegie Institution, to which we take this opportunity of extending our thanks.

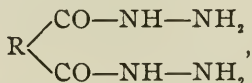
CHEMICAL LABORATORY,
JOHNS HOPKINS UNIV.,
December, 1904.

THE HYDRAZINE DERIVATIVES OF TETRACHLORPHTHALIC ACID.

BY ISAAC KING PHELPS.

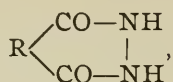
At the suggestion of Professor Theodor Curtius, the following investigation of hydrazine derivatives of tetrachlorphthalic acid was undertaken. A considerable part of the work was done in the laboratory of the University of Heidelberg, in the summer semester of 1902.

These hydrazine derivatives of tetrachlorphthalic acid appear to follow the typical reactions of hydrazine derivatives of organic dibasic acids,¹ in general methods of formation, giving substances of the primary type,



and also the usual secondary hydrazides of the type

¹ Curtius, Schöfer and Schwan : J. prakt. Chem., **51**, 187 (1895). Curtius and Foersterling : *Ibid.*, **51**, 371 (1895).



with characteristic acid properties. Both classes of derivatives of this acid are characterized by high melting-point, stability and inertness.

The neutral ester of tetrachlorphthalic acid, prepared by acting upon the silver salt of the acid with ethyl iodide and crystallizing from alcohol, reacts very slowly with hydrazine hydrate. The product proved to be the primary hydrazide of the acid, combined with 1 molecule of hydrazine. In general, the primary hydrazides¹ of organic dibasic acids are basic in properties, forming compounds with 2 molecules of a monobasic acid, but the primary hydrazide of tetrachlorphthalic acid shows acidic power in combining, as it does, with the strongly basic hydrazine. Further, the substance so formed is quite stable toward heat, showing an effect first at 290°; by treatment with aqueous hydrochloric acid it loses the molecule of hydrazine of combination, but does not take up halogen acid, even when treated with acid of 1.20 sp. gr.

The acid ester of tetrachlorphthalic acid was prepared by boiling tetrachlorphthalic acid with absolute alcohol. When this product was treated with hydrazine hydrate the reaction was slow, resulting finally in the formation of a number of substances. Although tried under varying conditions, no definite new derivatives were isolated.

By treating tetrachlorphthalic acid with hydrazine hydrate and heating, the secondary hydrazide results. It is also a stable substance, acts as a weak monoacidic base and dissolves in aqueous potassium or sodium hydroxide solutions, but not in sodium carbonate or ammonium hydroxide solutions.

EXPERIMENTAL.

Primary Hydrazide Combined with Hydrazine,
 $\text{C}_6\text{Cl}_4(\text{CONHNH}_2)_2 \cdot \text{N}_2\text{H}_4$.—Diethyl tetrachlorphthalate (0.75 gram) was heated with 0.26 gram of hydrazine hydrate (b. p. 119°) (1 mol. : 1 mol.) with 1 cc. of ether, in a sealed tube, at

¹ *Loc. cit.*

100°, for 10 hours. The yellow crystals which had separated were filtered off and washed with ether, in which they were insoluble; from the filtrate and ether washings 0.5 gram of solid material was obtained which was crystallized once from alcohol and was recognized by the melting-point, 59°, as composed chiefly of unchanged ester. The yellow, crystalline material, insoluble in ether, was found to be slowly and difficultly soluble in hot alcohol, from which it crystallized, on cooling, in fine, feathery needles. It charred slowly at 290°–300°, without melting. Analysis:

0.0812 gram substance gave 17 cc. moist N at 20° and 755.6 mm.

	Calculated for $C_6H_{10}O_2Cl_4N_6$.	Found.
N	23.12	23.81

Primary Hydrazide, $C_6Cl_4(CONHNH_2)_2$.—The hydrazine salt of the primary hydrazide above described was treated with a hot alcoholic solution of hydrochloric acid, in excess and boiled; the yellow substance lost its color but remained insoluble. It was filtered off, washed and dried *in vacuo*. It was insoluble in the common organic solvents and also in concentrated hydrochloric acid. Analysis:

0.1849 gram substance gave 29 cc. moist N at 23° and 758 mm.

	Calculated for $C_6H_6Cl_4O_2N_4$.	Found.
N	16.90	17.63

Secondary Hydrazide, $C_6Cl_4(CONH)_2$.—Tetrachlorophthalic acid (5 grams) and hydrazine hydrate (1.23 grams) (1 mol : 1.5 mol.) were heated together under a return condenser, in an oil-bath, at 140°–150° for half an hour. The cooled, slightly yellow residue was thoroughly extracted with hot water. The product was insoluble in the common organic solvents—excepting only glacial acetic acid, from which it was obtained in pale yellow crystals, on cooling the hot solution. It melted, with slight decomposition, at 286°–287° and dissolved in aqueous sodium and potassium hydroxide solutions, from which it was precipitated, unchanged, by acids. Analysis:

0.1774 gram substance gave 14.8 cc. moist N at 21° and 754 mm.

	Calculated for $C_8H_2O_2N_2Cl_4$.	Found.
N	9.36	9.42

0.1673 gram substance gave 0.3161 gram AgCl (Carius).

	Calculated.	Found.
Cl	46.85	47.28

The Diacetyl Derivative, $C_6Cl_4(CONCOCH_3)_2$.—The secondary hydrazide (2 grams) and acetic anhydride (4 grams) (1 mol. : 6 mol.) were boiled for 3 hours, under a return condenser. The solid material, formed on cooling, was crystallized twice from alcohol. It melted at 203°–204°. Analysis :

0.1690 gram substance gave 11 cc. moist N at 17° and 755 mm.

	Calculated for $C_{12}H_6O_4N_2Cl_4$.	Found.
N	7.32	7.50

The Sodium Salt of the Secondary Hydrazide, $C_6Cl_4(CON)_2HNa$.—The crude, secondary hydrazide (3 grams) was dissolved in a slight excess of sodium hydroxide solution, precipitated with aqueous hydrochloric acid and washed carefully on a filter. The freshly prepared material was treated with sodium hydroxide solution, made by treating the metal with alcohol and diluting with water, in amount insufficient to dissolve it. The excess of the hydrazide was filtered off, the filtrate evaporated and, finally, the solid dried in a vacuum, over sulphuric acid. Analysis :

0.2520 gram salt gave 0.0546 gram Na_2SO_4 .

	Calculated for $C_6HCl_4O_2N_2Na$.	Found.
Na	7.16	7.02

The Potassium Salt of the Secondary Hydrazide, $C_6Cl_4(CON)_2HK$.—The potassium salt was similarly prepared—with the single exception that commercially pure hydroxide was used, instead of that obtained from the metal. This product differed from the sodium salt in being slightly more readily soluble in water. Analysis :

0.2153 gram salt gave 0.0551 gram K_2SO_4 .

	Calculated for $C_6HCl_4O_2N_2K$.	Found.
K	11.58	11.49

The Silver Salt of the Secondary Hydrazide,
 $C_6Cl_4(CON)_2HAg$.—The sodium salt was dissolved in water and treated with a slight excess of a solution of silver nitrate. The white precipitate was filtered off, washed carefully with water and dried in darkness, over sulphuric acid, in a vacuum. Analysis :

0.1198 gram salt gave 0.0413 gram $AgCl$.

	Calculated for $C_6HCl_4O_2N_2Ag$.	Found.
Ag	26.50	26.95

Ethyl Carboxylate of the Secondary Hydrazide,
 $C_6Cl_4(CON)_2HCOOC_2H_5$.—A mixture of 2 grams of the silver salt with 10 cc. of ethyl chlorcarbonate was boiled under a return condenser, for 8 hours ; the excess of ester was allowed to evaporate spontaneously and the solid residue extracted with hot alcohol. The white, prismatic crystals, which appeared on cooling the solution, melted at 244° – 245° . Analysis :

0.1420 gram substance gave 9.9 cc. moist N at 20° and 760.5 mm.

	Calculated for $C_{11}H_6O_4Cl_4N_2$.	Found.
N	7.55	7.98

Although, in the benzene nucleus of the compounds above described, chlorine is fully substituted and although hydrazine hydrate is a strong base, in no case was an indication observed of a reaction between the hydrazine and the halogen in the ring.

The author gratefully acknowledges his indebtedness to Professor Theodor Curtius for many helpful suggestions.

KENT CHEMICAL LABORATORY,
 NEW HAVEN, CONN.

AN ELECTRICAL METHOD FOR THE COMBUSTION OF ORGANIC COMPOUNDS.

BY H. N. MORSE AND L. S. TAYLOR.

The process for the analysis of organic compounds, which is here described, has been in general use in this laboratory during the past year and with such satisfactory results that it has almost wholly supplanted the older method of burning organic compounds. It has already been applied to the combustion of hydrocarbons and their oxygen, halogen, nitrogen and sulphur derivatives. The advantages which it has been found to possess, over the usual method, are the following: (1) The apparatus required is so compact and of such small dimensions, that the combustions can be made at the working table of the student; (2) the waste of heat energy is much smaller; (3) the time consumed in preparing for and in making a combustion is considerably diminished.

Fig. I. (p. 594) represents the apparatus in its simplest form. The thin glass combustion tube is closed at one end and has a length of 350 mm. and an internal diameter of 15 mm. Through the rubber stopper in its open end there pass: (1) The porcelain tube *c*, which has a length of 250 mm. and a diameter of 6 mm.; (2) the glass tube *k*, through which the products of combustion enter the absorption apparatus; (3) the rather stout platinum wire (No. 18 B & S gauge), which extends from *f* to *j*. The porcelain tube *c* is joined outside of the stopper, by means of rubber tubing, to the branched glass tube *d*. The latter is provided with a stopper, *g*, through which passes the platinum wire *e* (also No. 18), which extends into the porcelain tube to the point *h*, where it is joined to a smaller platinum wire (about No. 29, B & S gauge). The smaller wire has a length of about 1.75 meters and weighs, approximately, 2.5 grams. It extends, from its junction with the larger wire at *h*, through the porcelain tube to the inner end of the latter and then returns on the outside, in a series of suspended coils, to the point *j*, where it joins the larger wire *f*. Thicker wire is used from *f* to *j* and from *e* to *h* in order to avoid any overheating of the rubber stopper by the current.

The roll of copper wire gauze *b*, about 60 mm. in length, is inserted between the end of the porcelain tube and the boat containing the substance to be burned.

The oxygen or air, which is used in the combustion, enters the apparatus at *d* and while passing over the portion of the small wire which is within the porcelain tube, has its temperature raised more or less, according to the rate of its flow. It is, therefore, already hot when it enters the tube *c*, where the combustion is to be effected. The excess of the oxygen and the products of the combustion pass together over the heated coils on the outside, completing the burning of any unoxidized material coming from the rear.

In the earlier work with this apparatus we employed stems of long clay tobacco pipes, but, owing to the highly porous character of this material, it was found necessary, in order to obtain satisfactory determinations of hydrogen, to dry out the tube each time before beginning a combustion. We afterwards substituted for the pipe stems unglazed porcelain tubes, which were made for us at the Royal Berlin Porcelain Works. These have proved very durable and they are not, of course, hygroscopic to an appreciable degree. None of these porcelain tubes has yet cracked, though some of those in use have served for more than a hundred combustions.

The roll of copper wire gauze, *b*, is not absolutely necessary when the substances to be burned do not readily yield explosive mixtures with oxygen and, in our earlier work, it was omitted. Its presence is, however, of advantage because much less care is required in the management of the combustion with it than without it. If the substances are liquids, or if they readily yield large quantities of inflammable vapors when heated, the roll of wire gauze must be inserted between the material and the end of the porcelain tube through which the oxygen enters. There is one objection and only one, to its use, this is that the flow of oxygen or air must be continued for some time after the completion of the combustion, in order to insure the removal of all of the carbon dioxide and water from the space occupied by the boat.

The combustion is conducted in the following manner: Having placed, in the positions indicated in the figure, the boat containing the material and the roll of copper wire gauze (which, in the beginning, may or may not be oxidized) and having joined the tube *k* to the usual train of absorption apparatuses, a slow current of dry and purified oxygen is admitted and the electric circuit is closed through a regulating rheostat. The flow of the current is gradually increased until the wire coils assume a bright red color, then the roll of gauze, *b*, is heated by means of a gas lamp giving a broad, thin flame, to a temperature at which the copper is readily oxidized by the hot oxygen issuing from the porcelain tube. The substance in the boat is then heated with the same lamp, or with another which is held in the hand. The rate of heating and the flow of oxygen are so regulated with respect to each other that at least one-half of the roll of wire gauze is kept in the oxidized condition during the entire combustion. After the formation of volatile products has ceased, the reoxidation of the copper progresses rapidly and the oxygen enters the rear compartment, burning any residue of carbon in the boat or upon the glass. Having finished the combustion of the substance, the current of oxygen is replaced by one of dried and purified air, the flow of which must, of course, be continued until the products of combustion have all been expelled from the space behind the roll of wire gauze. It is here that a miscalculation is likely to be made. The time required for the complete removal of these products depends, principally, upon the freedom of diffusion through the gauze and for this reason it should not be rolled too tightly.

The apparatus, as already described, is adapted to the combustion of those solids and liquids which consist of carbon and hydrogen, or of carbon, hydrogen and oxygen.

The heating of the roll of wire gauze *b*, and, at times, of the substance also, is facilitated by inverting over the tube, at a little distance above it, a trough of asbestos board, the side of the trough, at the back, being much deeper than that in front. This arrangement is supported in its position by a rod, which

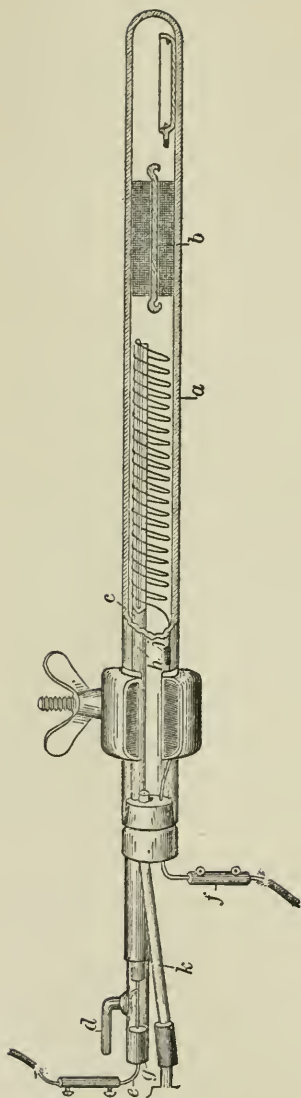


Fig. I.

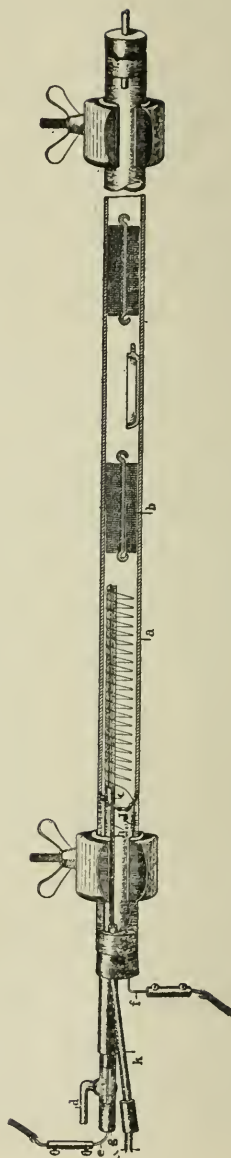


Fig. II.

is inserted in a heavy block, resting upon the work table behind the tube. The device is also of advantage in protecting the tube from draughts of cold air during the combustion and during the subsequent cooling period. The portion of the glass tube which is occupied by the porcelain tube and the platinum wire is protected, on the bottom, by a semi-circular strip of asbestos board which is inserted in the clamp between the lower jaw and the glass. To protect the upper portion of the tube in the same region, a semi-circular trough of mica is inverted over it, behind the clamp, in such a manner that the lower edges of the mica rest in the asbestos trough below. The mica is made to keep its curved form by riveting it to narrow strips of metal and then bending the latter to the required shape.

The cooling of the tube requires some care. The current should be reduced quite gradually and it is well, also, as soon as the combustion is finished, to cover the portions of the glass tube which is beyond the porcelain one with the soot from a smoky flame and to take any other measures for the protection of the tube which will contribute toward the proper annealing of the glass. Care must likewise be taken never to allow the platinum loops to come in contact with the glass either while heating or cooling the tube, because, in the former case, the metal is likely to stick to the glass, while, in the latter, the tube is quite sure to crack at some lower temperature. If the loops are too large, the wire should be taken out and rewound.

The time required for a combustion does not, ordinarily, exceed half an hour and it may be reduced to 20 minutes, or even less, if the substance to be burned is of such a character that the roll of wire gauze can be dispensed with. We do not, however, recommend its omission at any time, except to those who have had some experience with the method.

The consumption of electrical energy is small, amounting to about 3.6 amperes at 54 volts (194.4 watts, or one-third of a horse power) during the time when the highest temperature is maintained.

At the highest temperatures employed during the combustion (at a bright red, but not a white heat), especially when

the wire is new, there is a sensible volatilization of the platinum. This volatilization of platinum in an atmosphere of oxygen, at comparatively moderate temperatures, has been repeatedly noticed by others. In one case, a platinum wire weighing, in the beginning, 2.3446 grams was found, at the end of the thirty-eighth combustion, to have lost 0.1337 gram in weight. The volatilized metal settles upon the surfaces of the glass and porcelain tubes as a dark deposit which, at first, may be mistaken for carbon. The presence of such films of volatilized platinum upon the inner surface of the tube is, of course, of some assistance in the combustion.

The obvious objections to the use of the short closed combustion tube represented in Fig. I. are the following: In the first place, whenever the boat is to be introduced or withdrawn, it is necessary to remove and reinsert the rubber stopper with the tubes and wires which pass through it and also the roll of wire gauze and, during such manipulation, the wire loops, which should be distributed uniformly along the porcelain tube, are easily displaced and may become entangled. Again, as previously mentioned, the flow of air must be continued for some time after the combustion is otherwise finished, in order to insure the complete removal of carbon dioxide and water from the space occupied by the boat. These difficulties are wholly obviated by using a somewhat longer tube which is open at both ends, as represented in Fig. II. In this arrangement the boat is introduced from the rear and there is placed behind it a second roll of copper wire gauze. The stopper in the front end of the combustion tube, the forward roll of wire gauze and also the apparatus as a whole, are never disturbed. Each roll of wire gauze is heated by a lamp giving a broad, thin flame and there is inverted over both rolls and the space between them the asbestos shield already described. The lamps should be raised until the bottom of the tube is just within the blue region of the flames. To prevent any sagging of the combustion tube while hot, it is supported at a point beneath the end of the porcelain tube by a forked or notched standard, which is placed under the asbestos trough in which the front portion of the apparatus lies.

The combustion is conducted in much the same manner as in the short closed tube, except that a slow current of air or oxygen is admitted from the rear during the entire experiment. This prevents any accumulation of volatilized matter in the back part of the tube and aids in the expulsion of the products of combustion from the space occupied by the boat.

If the substance to be burned is very volatile, it is advisable to introduce air and not oxygen at the rear and to employ, behind the boat, a roll of gauze which is only partially oxidized. In this way the vapors of the substance may be diluted with nitrogen to any desired extent.

The clamp at the rear is required only as a support and it should not be made to grip the tube so tightly as to prevent the free movement of the latter, back and forth through the former.

In the following determinations of carbon and hydrogen in cane-sugar, which were made for the purpose of testing the method, the short closed tube was employed and the roll of wire gauze was omitted. A clay tobacco pipe stem served for the introduction of oxygen and the effect of its use is evident in the high percentages of hydrogen which were obtained in the first four analyses. In the last two analyses, in which normal quantities of hydrogen were obtained, the pipe stem was thoroughly burned out in a current of oxygen before beginning the combustion :

Weight of sugar. Gram.	Carbon found. Per cent.	Hydrogen found. Per cent.	Time occupied in combustion. Minutes.
0.1364	41.95	6.86	25
0.1188	42.03	6.63	18
0.1227	42.03	6.65	18
0.1382	42.07	6.73	18
0.1154	42.11	6.47	18
0.2809	42.03	6.46	45
Theoretical,	42.09	6.47	

The current at the highest temperature was 2.6 amperes at 48 volts.

Careful management is required, even in the combustion of such substances as sugar, when the roll of wire gauze is

omitted. On several occasions, when it was attempted to reduce the time consumed in the combustion to 15 minutes or less, small explosions occurred and the dilute solution of palladium chloride in the Geissler apparatus, which was always attached to the end of the absorption train, darkened in color. Hence the combustion tube was lengthened slightly and the roll of wire gauze previously mentioned was inserted between the boat and the end of the porcelain tube. Combustions of toluene and two of naphthalene were made with the modified apparatus with the following results :

Toluene.

Weight of substance. Gram.	Carbon found. Per cent.	Hydrogen found. Per cent.	Time occupied in combustion. Minutes.
0.1057	90.91	8.62	35
0.065	91.25	8.80	35
Theoretical,	91.24	8.76	

Naphthalene.

Weight of substance. Gram.	Carbon found. Per cent.	Hydrogen Found. Per cent.	Time occupied in combustion. Minutes.
0.1184	93.54	6.36	55
0.1252	93.49	6.39	55
Theoretical,	93.70	6.36	

During the first attempt to burn naphthalene a slight deposit of the substance collected in the front end of the tube. The length of the small platinum wire was, therefore, increased by about 0.5 meter, making its total length about 2 meters. No further difficulty was experienced in effecting complete combustions. With the lengthened wire, the electrical energy consumed, at the highest temperature, was 3.6 amperes at 65 volts. The wire was afterwards shortened until, with a current of 3.6 amperes, the fall in potential was 54 volts.

The analyses of naphthalene and benzene, which follow, were made with the apparatus represented in Fig. II.

Naphthalene.

Weight of substance. Gram.	Carbon found. Per cent.	Hydrogen found. Per cent.	Time occupied in combustion. Minutes.
0.1274	93.59	6.83	45
0.1340	93.50	6.80	30
0.1198	93.51	6.46	30
0.1249	93.57	6.36	35
Theoretical,	93.70	6.36	

Benzene.

Weight of substance. Gram.	Carbon found. Per cent.	Hydrogen found. Per cent.	Time occupied in combustion. Minutes.
0.0887	92.24	7.82	40
0.1474	92.28	7.80	75
0.1749	92.20	7.87	75
0.1334	92.18	7.66	75
Theoretical,	92.25	7.75	

The Combustion of Substances Containing Nitrogen.

For the determination of carbon and hydrogen in compounds containing nitrogen, there are placed in the combustion tube : (1) a roll, 100 mm. in length, of copper wire gauze which has been reduced in the usual way by methyl alcohol ; (2) a roll, 80 mm. in length, of wire gauze which has been well oxidized ; (3) the boat containing the substance ; (4) a short roll of wire gauze also well oxidized.

During the combustion each of the three rolls is heated by a burner giving a broad, thin flame, the last lamp serving also for heating the substance. The portion of the tube occupied by the copper is covered by a screen of asbestos board, to insure a sufficiently high temperature for the reduction of nitric oxide. The flow of oxygen through the porcelain tube is so regulated that only about one-quarter of the copper roll *b*, is oxidized, while at the rear it is admitted as rapidly as may be necessary to keep a portion of the second roll at all times in an oxidized condition.

No great difficulty has been experienced in successfully burning nitrogenous compounds, except in the case of nitro derivatives and even these gave good results after we adopted the practice of introducing into the boat, with the

substance, a quantity of loose copper oxide or finely divided silica.

By way of testing the applicability of the method to compounds containing nitrogen, analyses were made of urea, uric acid, orthonitrophenol and metadinitrobenzene. The results are given below :

Urea.

Weight of substance. Gram.	Carbon found. Per cent	Hydrogen found. Per cent.	Time occupied in combustion. Minutes.
0.1237	19.87	6.79	60
0.1542	20.03	6.78	70
0.1569	19.90	6.78	60
Theoretical,	19.96	6.70	

Uric Acid.

Weight of substance. Gram.	Carbon found. Per cent.	Hydrogen found. Per cent.	Time occupied in combustion. Minutes.
0.1947	35.64	2.68	75
0.1738	35.60	2.68	75
0.1970	35.65	2.62	
0.1929	35.60	2.42	
Theoretical,	35.67	2.39	

Nitrophenol.

Weight of substance. Gram.	Carbon found. Per cent.	Hydrogen found. Per cent.	Time occupied in combustion. Minutes.
0.2632	51.69	3.75	75
0.1520	51.62	3.89	75
0.1225	51.78	3.76	60
0.1315	51.78	3.76	70
0.1464	51.75	3.79	60
Theoretical,	51.77	3.62	

Dinitrobenzene.

Weight of substance. Gram.	Carbon found. Per cent.	Hydrogen found. Per cent.	Time occupied in combustion. Minutes.
0.1152	42.75	2.61	90
0.1435	42.70	3.02	120
0.1441	42.67	2.62	105
0.1174	42.72	2.78	120
0.1462	42.73	2.72	120
Theoretical,	42.83	2.39	

The time consumed in the burning of these nitrogenous compounds, especially of the dinitrobenzene, was probably greater than necessary ; but some of our earlier experiences had convinced us that, in order to secure a complete reduction of the nitric oxide, the carbon must be entirely burned before the products of the combustion reach the reduced roll *b*, of wire gauze.

The Combustion of Halogen Compounds.

To prepare the apparatus for the analysis of substances containing the halogens, a piece of silver foil, about 50 mm. in width, is rolled up with a sheet of thick paper, which is afterwards withdrawn. The silver roll is placed in the tube quite close to the end of the porcelain tube and is not directly heated during the combustion. In other respects the arrangements are the same as for the combustion of non-nitrogenous compounds. A roll of well oxidized copper wire gauze follows the one of silver, then the boat containing the substance and, finally, a second roll of oxidized copper wire gauze.

During the combustion there is formed a quantity of fusible cuprous-halogen salt, which deposits itself more or less upon the inner surface of the glass tube, but does not, at any time, get beyond the roll of silver foil into the space occupied by the porcelain tube and platinum wire. On cooling, the cuprous-halogen salt, in accordance with the well-known behavior of such compounds, absorbs large quantities of oxygen, only to give it up again when the apparatus is reheated in a succeeding experiment. At the same time the copper wire, in the oxidized rolls, grows thinner and becomes quite brittle.

The quantity of the cuprous salt accumulates, after a few combustions, to such an extent that the time required for its oxidation is considerable. Hence, it is well to cleanse the combustion tube frequently and to renew, at the same time, the oxidized rolls of copper wire gauze.

The substances selected for the purpose of testing the applicability of the method to halogen compounds were dibromobenzene and chloral ethylate. The results are given below :

Dibrombenzene.

Weight of substance. Gram.	Carbon found. Per cent.	Hydrogen found. Per cent.
0.1245	30.62	1.85
0.1395	30.40	1.82
0.1319	30.33	1.75
0.0836	30.40	1.93
0.0745	30.42	1.81
Theoretical,	30.51	1.71

Time of combustion about 30 minutes.

Chloral Ethylate,
 $\text{CCl}_3\text{CH}(\text{OH})\text{OC}_2\text{H}_5.$

Weight of substance. Gram.	Carbon found. Per cent.	Hydrogen found. Per cent.
0.1611	24.83	3.63
0.1765	24.90	3.64
0.1789	24.61	3.71
0.1570	24.73	3.83
Theoretical,	24.82	3.64

Time of combustion about 30 minutes.

The Combustion of Sulphur Compounds.

The determination of carbon and hydrogen in compounds containing sulphur presents no difficulty. A large number of such analyses have been made in this laboratory within the past year and the results have been quite as satisfactory as those obtained by the older method. The only change which it is necessary to make in the simple arrangement for non-nitrogenous and non-halogen compounds, in order to adapt the method to the combustion of sulphur compounds, is to substitute lead chromate for the roll of oxidized copper wire gauze which is nearest to the end of the porcelain tube. Instead of maintaining the lead chromate in its position in the tube by means of plugs of asbestos or of wire gauze, it has been found more convenient and better for the glass tube to introduce it in the form of a cartridge. This is prepared by filling, with the loose, granular chromate, a shell made from fine copper wire gauze.

The first analyses of sulphur compounds were made with

diphenylsulphone as the material. The results are given below :

Weight of substance. Gram.	Carbon found. Per cent.	Hydrogen found. Per cent.	Time occupied in combustion. Minutes.
0.1035	65.93	4.63	30
0.0997	66.00	4.70	45
0.1021	65.89	4.73	60
0.0961	65.98	4.53	45
Theoretical,	66.01	4.61	

JOHNS HOPKINS UNIVERSITY,
March 1, 1905.

Contribution from the Chemical Laboratory of the University of Illinois.

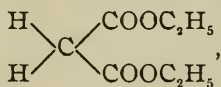
A CONVENIENT AND PRACTICAL METHOD FOR MAKING THE ESTER OF MESOXALIC ACID.

BY RICHARD SYDNEY CURTISS.

At present there exists no good and easy method for the preparation, in quantity, of diethyl mesoxalate. The two ways of making it, as given by Beilstein, are : (a) The distillation of acetylbromtartronic ester ;¹ (b) the action of ethyl iodide on silver mesoxalate.² Both are costly methods.

Bouveault and Wahl³ have, more recently, discovered that it can be obtained by the action of nitric oxide on diethyl isonitrosomalonnate. The yield is not given.

This difficulty in its preparation has resulted in a search for some other method which would give a good yield, at a less cost in time and material. Manifestly the simplest way, theoretically possible, to make diethyl mesoxalate is to convert the two methylene hydrogen atoms of malonic ester,



into hydroxyl groups.

It has been found that this can be accomplished easily, by

¹ Conrad and Brückner : Ber. d. chem. Ges., 24, 3000.

² Petrief : J. russ. chem. Ges., 10, 75.

³ Compt. rend., 137, 196.

saturating the ester, at -15° , with the gaseous red oxides of nitrogen, obtained from arsenic trioxide and nitric acid and filtering off the crystals, which are deposited in fair quantity, after the mixture has stood a few hours.

This product, once recrystallized, is pure diethyl mesoxalate, as shown by its melting-point, 57° , its analysis, the formation of a potassium salt by saponification and of a yellow phenyl hydrazone from the latter, corresponding in melting-point to that of the phenyl hydrazone of mesoxalic acid.

The above treatment of diethylmalonate leads to the formation of a number of other products. A study of these, the use of other oxidizing agents and also of the various reactions of mesoxalic ester as a ketone is in progress.

URBANA, ILL.,
April 8, 1905.

ON THE PINACONE-PINACOLIN REARRANGEMENT.

BY P. J. MONTAGNE.

The preliminary publication by Acree¹ induces me to make the following remarks:

Acree discusses the question, whether the pinacone-pinacolin, or other similar rearrangements, can take place through ring formation, as first suggested by Coutourier and subsequently by others. This suggestion being applied to aromatic derivatives, the group in the nucleus would prove, in that case, to have changed its position after the reaction. Acree intends to determine the position of the group in the nucleus before and after the migration and to solve the question in that way.

In April, 1901, however, I treated this same question at the "Nederlandsch Natuur-en Geneeskundig Congres" at Rotterdam (Dutch Physical and Medical Congress) and solved it with respect to two examples. Two articles on this subject have been published.² I have ascertained that, in the case of benzil, as well as of hydrobenzoin, the group in the nucleus does not change its position after the migration, a ring formation, being, consequently, impossible. In view of an

¹ This JOURNAL, 33, 180 (1905).

² Rec. Trav. Chim., 21, 6, 30.

explanation given by Nef, I announced, in the article above mentioned, the solution of this problem for the benzpinacone. As the result of my investigation of the subject, I stated that, in the rearrangement of this substance, the group in the nucleus retained its place. This article has recently been published.¹

I am trying now to solve the same problem in the case of other compounds.

DEVENTER, HOLLAND,
April, 1905.

REVIEWS.

A SELECT BIBLIOGRAPHY OF CHEMISTRY, 1492-1902. By HENRY CARRINGTON BOLTON. Second Supplement. Smithsonian Miscellaneous Collections. Part of Vol. XLIV. Washington: Smithsonian Institution. 1904. pp. 462.

Dr. Bolton's premature death occurred while this work was in the press, consequently Mr. Axel Moth compiled the index and prepared most of the proof. The original volume appeared in 1893; the first supplement, published in 1899, included the literature from 1892 to the close of 1897; the present volume brings it down to the end of 1902. No attempt has been made to index books and periodicals, but the titles of books are given under the following heads: (I.) Bibliography, (II.) Dictionaries, (III.) History, (IV.) Biography, (V.) Chemistry, pure and applied, (VI.) Alchemical literature of the nineteenth century, (VII.) Periodicals, (VIII.) Academic dissertations. The volume shows evidence of the painstaking care characteristic of Dr. Bolton's work and will, undoubtedly, be of considerable utility to many chemists.

J. B. T.

DIE WISSENSCHAFTLICHEN GRUNDLAGEN DER ANALYTISCHEN CHEMIE. Elementar dargestellt von W. OSTWALD. Vierte auflage. Leipzig: Engelmann. 1904.

Prof. Ostwald's valuable little book has appeared in English, Russian, Italian, Hungarian, Japanese and French translations. It would be superfluous to add anything to what has been said of it in the review of the first edition² and the review of M'Gowan's translation.³

E. R.

¹ Rec. Trav. Chim., **24**, 105 (1905).

² THIS JOURNAL, **16**, 564.

³ Ibid., **18**, 523.

OUTLINES OF PHYSIOLOGICAL CHEMISTRY. By S. P. BEEBE, PH.D., Physiological Chemist to the Huntington Fund for Cancer Research, and R. H. BUXTON, M.D., Professor of Experimental Pathology, Cornell Medical College. New York: The Macmillan Company. 1904. pp. 194. Price, \$1.50.

This book was intended to fill a gap left by the laboratory manuals and was written to aid the student in grasping the theoretical aspect of physiological chemistry. That there is a place for such a book the reviewer does not deny, but that the present effort is certainly not a successful one is beyond question. In a few pages are considered: The Theory of Solutions (22 pp.); Organic Chemistry (77 pp.); The Proteids (61 pp.); The Enzymes (15 pp.); Diseases and Immunity (16 pp.). The authors explain the use of the tartrate in Fehling's solution as follows: "To avoid this, tartaric acid is used, which forms a soluble colorless (?) compound with the cupric oxide but does not affect the red cuprous oxide. The point is to add something by which the CuO is made soluble and colorless, but which leaves the Cu_2O unchanged."

On page 174 the statement is made that the oxygen, liberated from oxyhaemoglobin, is atomic and not molecular oxygen. Innumerable other examples might be given but they all show the same thing. If the contents of the book had been better it would have deserved a better style. The fact that the authors state in the preface that they hope no errors had been committed, proves that this was not sufficient to exclude them.

A. S. L.

NOTES ON ASSAYING AND METALLURGICAL LABORATORY EXPERIMENTS. By RICHARD W. LODGE. New York: John Wiley & Sons. 1904. 8vo. pp. viii + 287. Price, \$3.00.

The topics considered are: Reagents, furnaces, crucibles, etc.; Sampling; The assays of ores of silver, of gold, of lead; The assay of bullion; The assay of ores of copper and tin; Platinum and the platinum group; Metallurgical laboratory experiments and notes.

The book, as a whole, is a valuable addition to the existing literature on assaying, which is, as defined by the author, a branch of analytical chemistry. It will prove of use to practical assayers and will tend to make them discard the rule-of-thumb methods which have too long prevailed. As a textbook the arrangement of the subject-matter is bad; silver in ores is treated in a separate chapter from gold in ores; copper matte is the first assay given in detail; the assay of bullion is placed between the assay for lead and for copper, etc. Many valuable tables are given, such as the losses of silver in cupellation at different temperatures. The explanations of the ef-

fect of fluxes, especially the use of iron in crucible assays and the addition of silica in scorification, are excellent. Many points admit of criticism, such as the inclusion of the scorification method for telluride ores and the Cornish method for copper, with the exclusion of the Gay-Lussac method for silver bullion. Experiments by students are given in tiresome detail, often without any particular conclusions being drawn from them, while the journal articles, on similar lines, are ignored. Though many of the subjects treated in the old works on assaying are very properly omitted, some, of importance at present, such as corrected assays, the sampling of pig copper and the assay of cyanide solutions, are not adequately treated.

E. H. M.

A LABORATORY CHEMISTRY. By RICHARD B. MOORE, Instructor in Chemistry, University of Missouri. Philadelphia: J. B. Lippincott Co. 1904.

This is a little manual intended for use in high schools. In the preface the author says: "In some of our states the text-books in chemistry, prescribed by law for the secondary schools, are extremely unsatisfactory. In such cases a laboratory manual that is a little more than a laboratory manual will have a distinct use." It is largely for this reason that the chapters on theory have been introduced.

The selection of experiments is judicious and the explanatory text is clear and simple.

E. R.

HIGH-TEMPERATURE MEASUREMENTS. By H. LE CHATELIER and O. BAUDOUARD. Authorized translations and additions by G. K. BURGESS. Second edition, revised and enlarged. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1904. pp. 341. Price, \$3.00.

The appearance of the English translation of this book has already been referred to.¹ The second edition contains new matter pertaining to Optical Pyrometry, Electrical Resistance and Thermoelectric and Gas Pyrometry. The translator states that brief descriptions have been added of some other pyrometers which have been considerably used in the industries, especially in the United States. The importance of standardizing pyrometers has been emphasized by a special chapter devoted to that subject.

H. C. J.

THE ELECTRIC FURNACE. By HENRI MOISSAN, Membre de l'Institut, Professor of Chemistry at the Sorbonne. Translated by A. T. DE MOUILPIED, B.Sc. (Lond.), M.Sc. (Vict.), Ph.D., Assistant Lecturer in Chemistry in the University of Liverpool. London: Arnold; New York: Longmans, Green & Co. 1904. Price, \$2.75.

A review of Dr. Victor Lenher's translation of Moissan's

¹ THIS JOURNAL, 27, 235.

"Four Electrique" appeared quite recently,¹ so that further discussion of Moissan's book is unnecessary and attention may be confined to the respective merits of the translations.

Even a very superficial examination leads to the conclusion that Dr. de Moulpiéd writes better and clearer English than Dr. Lenher and, on closer observation, we find that some passages, which were obscure in Lenher's translation, have lost their obscurity in that of Moulpiéd. Both translations are authorized and prefaced by Moissan. The English book has better type and paper than the American. E. R.

DIE DARSTELLUNG DES ZINKS AUF ELECTROLYTISCHEN WEGE, mit 59 Abbildungen. By DR. EMIL GÜNTHER. Leipsic: W. Knapp. 1904. pp. xii + 246. Price, M. 10.

This book forms Volume XVI. of the "Monographs on Applied Electrochemistry," edited by V. Engelhardt, chief engineer and chief chemist of the firm of Siemens and Halske. The author, well known by his papers on electrometallurgical subjects, has had practical experience in the electrolytic treatment of zinc ores and is, therefore, well fitted to write upon the subject.

In the preface he briefly reviews the history of the electrometallurgy of zinc. Although many investigations were carried out during the years 1880-1895, to find new methods and to perfect old ones, the interest seems to have lagged since that time and to-day there is only a single plant in active operation.² While the difficulties that have to be overcome are much greater than those encountered at first in the electrolytic refining of copper, the author believes that, with a more intelligent application of physical chemistry to metallurgical problems than has been so far the case, there will come a brighter future for the electrometallurgy of zinc. While this is to be hoped for, the main obstacle to the prospect lies in the advance that has been made in the mechanical concentration of ores.

A closer study of the principles of regular wet ore-dressing has resulted in the construction of improved machinery and magnetic concentration has become an important factor in the treatment of mixed sulphide ores; static machines, of much promise, are coming into use and, more recently, acid treatment, combined with flotation, is making available immense heaps of ores which have been thrown over the dump as waste material. If the prospects for the electrometallurgy of zinc are not very brilliant, this mode of treatment may find more application than at present in special cases with ores, while

¹ THIS JOURNAL, 32, 406.

² Brunner, Mond & Co., Northwich, England.

electrolytic refining of crude zinc will hardly be revived. It is of value, however, to have a book devoted to the subject.

In the introduction (pp. 1-20) there are discussed, briefly, the properties, statistics and uses of zinc and the common methods of smelting its ores. The electrolytic chapter has wet (pp. 24-180) and dry (pp. 180-208) treatment as its two main divisions. Under wet electrolysis there are two classes of processes, those in which the anode energy is utilized and those in which it is not; under dry electrolysis, the divisions are preparation of electrolyte and form of apparatus. Under each head there have been assembled the various processes that have been patented or carried out more or less experimentally. Each is briefly criticized, as far as this is possible from the available data. The Hoepfner chloride process, the only one that has any commercial interest at present, occupies 91 pages of the 150 given to wet electrolysis. The discussion is of special value, as the author was actively engaged in carrying out this process in Germany. The appendix (pp. 211-241), giving an estimate of the cost of a Hoepfner plant and the cost of working, has value in that it furnishes an excellent basis for making similar estimates for other countries.

The book does not aim to discuss the principles of the electrodeposition of zinc; it treats of processes and, incidentally, in its *critique* applies the general principles and explains the difficulties. The general arrangement is good, the matter is clearly presented, references are given to sources of information, there is an excellent table of contents and a satisfactory index. The book is well printed and can be recommended to all interested in the subject.

H. O. HOFMAN.

THE BECQUEREL RAYS AND THE PROPERTIES OF RADIUM. By HON. R. J. STRUTT, Fellow of Trinity College, Cambridge. London: Eduard Arnold. 1904. pp. 214. Price, \$2.40, net.

This is an admirable book on radio-activity, from the semi-popular standpoint. The author states in his preface that "In writing this book my object has been to give as clear and simple an account of the phenomena of radio-activity as the subject admits of, without sacrificing accuracy. The extraordinary properties of radium have excited general interest outside the scientific world and there are probably many who would be glad to learn something of the subject, if they could find it explained without the use of technicalities. However essential mathematical methods may be in developing the subject, they are seldom really necessary in presenting the results. Moreover, some idea of the train of reasoning can generally be given in ordinary language."

This gives an admirable idea of the aim of the work. The scope is fairly comprehensive, including chapters on: Electric Discharge in High Vacua, Discovery of Radio-Activity, The Properties and Nature of the Radiations, Absorption and Ionization, The Changes Occurring in Radio-active Bodies, Radio-activity in the Earth and in the Atmosphere, the Ultimate Products of Radio-active Change and The Electrical Theory of the Nature of Matter.

The book contains three appendices. The first describes a number of interesting and important experiments. The second is a brief theoretical discussion of the Theory of the Magnetic and Electrostatic Deflection of the Cathode Rays, or the β -Rays of Radio-active Substances. The third appendix deals with the treatment of pitchblende residues on a large scale.

The book is written in an enthusiastic and attractive style and holds the interest of the reader from beginning to end. A few sentences, however, could be revised advantageously, from the standpoint of English. On page 14 we read "and it is not possible to measure the electric charge of the cathode particles in a vacuum tube *either*." On page 99, "The most that can be done is to apply an electric force large enough to *snatch* practically all the ions, etc." On page 142, "clay soils are usually the most active, but Professor J. J. Thomson has found the sand from the beach at Whitby to be very active *too*."

There will doubtless be a large demand for the book, on account of the general popular interest in the subject and because it comes from an authoritative source. H. C. J.

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$C_{10}H_7BrMg$.	α -Naphthylmagnesium bromide. <i>Kohler and Heritage</i>	160
$C_{10}H_7BrMg$.	α -Naphthylmagnesium bromide. <i>Kohler and Johnstin</i>	44
$C_{10}H_7BrMg$.	α -Naphthylmagnesium bromide. <i>Kohler and Reimer</i>	349
$C_{10}H_8O_2N_2$.	5-Phenyluracil. <i>Wheeler and Bristol</i>	460
$C_{10}H_8O_9N_5$.	5-Aminouracil picrate. <i>Wheeler and Bristol</i>	442
$C_{10}H_{10}ON_3$.	2-Oxy-6-anilinopyrimidine. <i>Wheeler and Bristol</i> ...	459
$C_{10}H_{13}ON$.	Ethylacetanilide. <i>Bacon</i>	84
$C_{10}H_{13}ON$.	β -Phenylbutyramide. <i>Kohler and Reimer</i>	353
$C_{10}H_{13}O_2N$.	Ethylbenzhydroxamic acid methyl ester. <i>Biddle</i> ..	63

4 X.

$C_{10}H_7N_3ClBr$.	2-Anilino-5-brom-6-chlorpyrimidine. <i>Wheeler and Bristol</i>	444
$C_{10}H_8ON_3Br$.	2-Anilino-5-brom-6-oxypyrimidine. <i>Wheeler and Bristol</i>	444
$C_{10}H_{15}ON_3S_2$.	2-Ethylmercapto-5-methyl-6-thionurethanepyrimidine. <i>Wheeler and Bristol</i>	452

C₁₁-GROUP.

$C_{11}H_{12}O_2$.	Ethyl cinnamate. <i>Kohler and Heritage</i>	28
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$C_{11}H_{12}O_3$.	Benzyl acetoacetate. <i>Bacon</i>	79
$C_{11}H_{14}O$.	Dimethylstyryl carbinol. <i>Kohler and Heritage</i>	28
$C_{11}H_{14}O_2$.	Benzyl isobutyrate. <i>Bacon</i>	96
$C_{11}H_{17}O_4$.	Ethyl trimethylhydroxyadipate lactone. <i>Noyes</i>	361

3 XI.

$C_{11}H_{16}O_2Br$.	Ethyl α -bromcinnamate. <i>Kohler and Johnston</i> ...	38
$C_{11}H_{12}O_2Br_2$.	Dibromphenylpropionic ester. <i>Kohler and Johnston</i>	43
$C_{11}H_{13}O_2N$.	α -Cyan- β -phenylbutyric acid. <i>Kohler and Reimer</i> ..	352
$C_{11}H_{13}O_3N$.	Methylphenylmethylmalonic monamide. <i>Kohler and Reimer</i>	352
$C_{11}H_{17}O_4N$.	Ethyl dimethylcyansuccinate. <i>Noyes</i>	358

4 XI.

$C_{11}H_6O_4N_2Cl_4$.	Ethyl carboxylate of the secondary hydrazide of tetrachlorophthalic acid. <i>Phelps</i>	590
$C_{11}H_{11}O_4NI_2$.	Monoacetyldiiodotyrosine. <i>Wheeler and Jamieson</i> .	371

5 XI.

$C_{11}H_{16}ON_3BrS_2$.	2-Ethylmercapto-5-brom-6-iminothioethylcarbonatepyrimidine. <i>Wheeler and Bristol</i>	455
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C₁₂-GROUP.

$C_{12}H_{10}$.	Diphenyl. <i>Kohler and Johnston</i>	43, 44, 45
$C_{12}H_{24}$.	Hydrocarbon from petroleum. <i>Mabery</i>	264
$C_{12}H_{24}$.	Hydrocarbon from petroleum. <i>Mabery and Palm</i>	254

2 XII.

$C_{12}H_8O_2$.	2-Phenylbenzoquinone. <i>Hill and Hale</i>	11
$C_{12}H_{10}O_4$.	Quinhydrone. <i>Torrey and Hardenbergh</i>	168
$C_{12}H_{23}Cl$.	Chloride of hydrocarbon from petroleum. <i>Mabery</i> ..	264

3 XII.

$C_{12}H_7O_7N_3$.	5,2',4',-Trinitro-2-oxydiphenyl. <i>Hill and Hale</i>	20
$C_{12}H_7O_7N_3$.	5,3,4'-Trinitro-2-oxydiphenyl. <i>Hill and Hale</i>	18, 19
$C_{12}H_5O_5N_2$.	5,3-Dinitro-2-oxydiphenyl. <i>Hill and Hale</i>	12
$C_{12}H_5O_5N_2$.	5,4'-Dinitro-2-oxy-diphenyl. <i>Hill and Hale</i>	19
$C_{12}H_9O_3N$.	5-Nitro-2-oxydiphenyl. <i>Hill and Hale</i>	8
$C_{12}H_9O_3N$.	1-Nitro-3-phenyl-4-keto- Δ 2,5-dihydrobenzol. <i>Hill and Hale</i>	2
$C_{12}H_{11}O_2N$.	Ethyl α -cyancinnamate. <i>Kohler and Reimer</i>	337

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$C_{12}H_{11}O_3N$.	Ethyl cyanbenzoylacetate. <i>Kohler and Reimer</i>	349
$C_{12}H_{12}ON_2$.	5,3-Diamido-2-oxydiphenyl. <i>Hill and Hale</i>	14
$C_{12}H_{11}ON$.	5-Amido-2-oxydiphenyl. <i>Hill and Hale</i>	11
$C_{12}H_{13}N_3S$.	2-Ethylmercapto-6-anilinopyrimidine. <i>Wheeler and Bristol</i>	459
$C_{12}H_{20}IAs$.	Phenyl triethyl arsonium iodide. <i>Dehn</i>	151

4 XII.

$C_{12}H_6O_4N_2Cl_4$.	Diacetyl derivative of the secondary hydrazide of tetrachlorophthalic acid. <i>Phelps</i>	589
$C_{12}H_7O_5N_2Na$.	Sodium salt of 5,3-Dinitro-2-oxydiphenyl. <i>Hill and Hale</i>	13
$C_{12}H_5O_3NNa$.	Sodium salt of 5-nitro-2-oxydiphenyl. <i>Hill and Hale</i>	9
$C_{12}H_{12}ON_2S$.	2-Ethylmercapto-5-phenyluracil. <i>Wheeler and Bristol</i>	460
$C_{12}H_{14}N_3ClS$.	2-Ethylmercapto-6-anilinopyrimidine hydrochloride. <i>Wheeler and Bristol</i>	458

C_{13} -GROUP.

$C_{13}H_{12}$.	Diphenyl methane. <i>Bacon</i>	71, 77
$C_{13}H_{24}$.	Hydrocarbon from petroleum. <i>Mabery</i>	271
$C_{13}H_{26}$.	Hydrocarbon from petroleum. <i>Mabery</i>	264
$C_{13}H_{26}$.	Hydrocarbon from petroleum. <i>Mabery and Palm</i>	255

2 XIII.

$C_{13}H_{10}O$.	Benzophenone. <i>Bacon</i>	73, 74
$C_{13}H_{10}O$.	Benzophenone. <i>Kohler and Heritage</i>	35
$C_{13}H_{10}O$.	Benzophenone. <i>Kohler and Johnston</i>	40, 42
$C_{13}H_{11}Br$.	Bromdiphenylmethane. <i>Bacon</i>	75
$C_{13}H_{12}O$.	Benzhydrol. <i>Bacon</i>	71
$C_{13}H_{12}S$.	<i>o</i> -Tolylphenylsulphide. <i>Weedon and Doughty</i>	416
$C_{13}H_{25}Cl$.	Chloride of hydrocarbon from petroleum. <i>Mabery</i> ..	265

3 XIII.

$C_{13}H_8OBr_2$.	<i>p</i> -Dibrombenzophenone. <i>Bacon</i>	76
$C_{13}H_8OS$.	Thioxanthone. <i>Weedon and Doughty</i>	394
$C_{13}H_8O_3S$.	Benzophenonesulphonc. <i>Weedon and Doughty</i>	407
$C_{13}H_9O_7N_3$.	5,2',4'-Trinitro-2-oxydiphenyl methyl ether. <i>Hill and Hale</i>	20
$C_{13}H_9O_7N_3$.	5,3,4'-Trinitro-2-oxydiphenyl methyl ether. <i>Hill and Hale</i>	17
$C_{13}H_{10}O_2S$.	<i>p</i> -Phenylsulphidebenzoic acid. <i>Weedon and Doughty</i>	424

$C_{13}H_{10}O_2S$.	Phenylthiosalicylic acid. <i>Weedon and Doughty</i>	392
$C_{13}H_{10}O_3S$.	Diphenylsulphoxideorthocarboxylic acid. <i>Weedon and Doughty</i>	395
$C_{13}H_{10}O_4S$.	Diphenylsulphoneorthocarboxylic acid. <i>Weedon and Doughty</i>	386
$C_{13}H_{10}O_4S$.	<i>p</i> -Phenylsulphonebenzoic acid. <i>Weedon and Doughty</i>	426
$C_{13}H_{10}O_5N_2$.	5,3-Dinitro-2-oxydiphenyl methyl ether. <i>Hill and Hale</i>	13
$C_{13}H_{10}O_5N_2$.	5,4'-Dinitro-2-oxydiphenyl methyl ether. <i>Hill and Hale</i>	18
$C_{13}H_{11}ONa$.	Sodium benzhydrol. <i>Bacon</i>	71
$C_{13}H_{11}O_3N$.	5-Nitro-2-oxydiphenyl methyl ether. <i>Hill and Hale</i>	10
$C_{13}H_{12}O_2S$.	<i>o</i> -Tolylphenylsulphone. <i>Weedon and Doughty</i>	418
$C_{13}H_{14}N_4S_2$.	2-Ethylmercapto-6-phenylthiourea pyrimidine. <i>Wheeler and Bristol</i>	451
$C_{13}H_{16}O_2N$.	Ethyl α -cyan- β -phenylbutyrate. <i>Kohler and Reimer</i>	351

4 XIII.

$C_{13}H_9O_3ClS$.	Diphenylsulphoneorthocarboxylic chloride. <i>Weedon and Doughty</i>	410
$C_{13}H_9O_3ClS$.	<i>p</i> -Phenylsulphonebenzoic chloride. <i>Weedon and Doughty</i>	427
$C_{13}H_9O_5NS$.	Mononitrodiphenylsulphoxideorthocarboxylic acid. <i>Weedon and Doughty</i>	400
$C_{13}H_{11}O_3NS$.	Diphenylsulphoneorthocarboxylamide. <i>Weedon and Doughty</i>	411
$C_{13}H_{11}O_3NS$.	<i>p</i> -Phenylsulphonebenzamide. <i>Weedon and Doughty</i>	428
$C_{13}H_{13}N_4BrS_2$.	2-Ethylmercapto-5-brom-6-phenylthioureapyrimidine. <i>Wheeler and Bristol</i>	454

 C_{14} -GROUP.

$C_{14}H_{12}$.	Stilbene. <i>Kohler and Johnstin</i>	43
$C_{14}H_{28}$.	Hydrocarbon from petroleum. <i>Mabery</i>	265
$C_{14}H_{28}$.	Hydrocarbon from petroleum. <i>Mabery and Palm</i>	255

2 XIV.

$C_{14}H_{10}O_4$.	Dibenzoyl peroxide. <i>Bacon</i>	75
$C_{14}H_{12}O$.	Desoxybenzoin. <i>Kohler and Reimer</i>	354
$C_{14}H_{12}O_2$.	Benzhydrol formate. <i>Bacon</i>	88
$C_{14}H_{12}O_2$.	Diphenyl acetic acid. <i>Bacon</i>	88

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$C_{14}H_{12}Br_2$.	Stilbene bromide. <i>Kohler and Johnstin</i>	42
$C_{14}H_{14}O$.	Benzyl ether. <i>Bacon</i>	95
$C_{14}H_{15}N$.	Dibenzylamine. <i>Clarke</i>	499
$C_{14}H_{18}O_2$.	Amyl cinnamate. <i>Kohler and Heritage</i>	28
$C_{14}H_{27}Cl$.	Chloride of hydrocarbon from petroleum. <i>Mabery</i> ..	267

3 XIV.

$C_{14}H_{11}O_3N$.	Dibenzhydroxamic acid. <i>Biddle</i>	62
$C_{14}H_{12}O_4S$.	Methyl diphenylsulphoneorthocarboxylate. <i>Wee-</i> <i>don and Doughty</i>	413
$C_{14}H_{13}O_3N$.	5-Nitro-2-oxydiphenyl ethyl ether. <i>Hill and Hale</i> ..	10

4 XIV.

$C_{14}H_{16}O_6N_2Mg$.	Ethyl magnesium cyanacetacetate. <i>Kohler and</i> <i>Reimer</i>	345
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C_{15} -GROUP.

$C_{15}H_{30}$.	Hydrocarbon from petroleum. <i>Mabery</i>	267
$C_{15}H_{30}$.	Hydrocarbon from petroleum. <i>Mabery and Palm</i>	256

2 XV.

$C_{15}H_{11}N$.	β -Phenylcinnamionitrile. <i>Kohler and Reimer</i>	344
$C_{15}H_{12}O$.	Benzalacetophenone. <i>Kohler and Heritage</i>	31
$C_{15}H_{12}O$.	Benzalacetophenone. <i>Kohler and Reimer</i>	351
$C_{15}H_{12}O$.	Phenylhydrindone. <i>Kohler and Heritage</i>	34
$C_{15}H_{12}O_2$.	β -Phenylcinnamic acid. <i>Kohler and Heritage</i>	34
$C_{15}H_{12}O_2$.	β -Phenylcinnamic acid. <i>Kohler and Johnstin</i>	39
$C_{15}H_{13}N$.	β,β -Diphenylpropionitrile. <i>Kohler and Reimer</i>	340
$C_{15}H_{14}O$.	Dibenzyl ketone. <i>Hill and Hale</i>	8
$C_{15}H_{14}O_2$.	Benzhydrol acetate. <i>Bacon</i>	77
$C_{15}H_{14}O_2$.	β,β -Diphenylpropionic acid. <i>Bacon</i>	83
$C_{15}H_{14}O_2$.	β,β -Diphenylpropionic acid. <i>Kohler and Heritage</i>	26, 30
$C_{15}H_{14}O_2$.	β,β -Diphenylpropionic acid. <i>Kohler and Reimer</i>	341
$C_{15}H_{22}O_7$.	Ethyl trimethylparaconylmalonate. <i>Noyes</i>	363
$C_{15}H_{29}Cl$.	Chloride of hydrocarbon from petroleum. <i>Mabery</i> ...	268

3 XV.

$C_{15}H_{11}OBr$.	α -Brombenzalacetophenone. <i>Kohler and Johnstin</i> .	40
$C_{15}H_{12}OBr_2$.	Benzalacetophenone bromide. <i>Kohler and Johnstin</i>	43
$C_{15}H_{13}O_2N$.	Diphenylbrompropionic acid. <i>Kohler and Heritage</i>	34
$C_{15}H_{14}O_4S$.	Ethyl diphenylsulphoneorthocarboxylate. <i>Weedon</i> and <i>Doughty</i>	413
$C_{15}H_{15}ON$.	β,β -Diphenylpropionamide. <i>Kohler and Reimer</i>	341

C₁₆-GROUP.

C ₁₆ H ₃₀ .	Hydrocarbon from petroleum. <i>Mabery</i>	272
C ₁₆ H ₃₂ .	Hydrocarbon from petroleum. <i>Mabery and Palm</i>	257

2 XVI.

C ₁₆ H ₁₁ O ₂ .	α -Cyan- β -phenylcinnamic acid. <i>Kohler and Reimer</i> ..	343
C ₁₆ H ₁₄ N ₄ .	2,6-Dianilinopyrimidine. <i>Wheeler and Bristol</i>	460
C ₁₆ H ₁₆ O ₂ .	Benzyl hydrocinnamate. <i>Bacon</i>	93
C ₁₆ H ₁₆ O ₂ .	Methyl β,β -diphenylpropionate. <i>Kohler and Heritage</i>	25
C ₁₆ H ₁₈ O ₂ .	Diphenyl ethyl glycol. <i>Acree</i>	193
C ₁₆ H ₂₂ O ₇ .	Trimethylparaconic anhydride. <i>Noyes</i>	364
C ₁₆ H ₂₄ O ₃ .	Oxidation product of abietic acid. <i>Endemann</i>	529
C ₁₆ H ₂₄ O ₄ .	Oxidation product of abietic acid. <i>Endemann</i>	527

3 XVI.

C ₁₆ H ₁₃ O ₂ N.	Cyandiphenylpropionic acid. <i>Kohler and Reimer</i> ..	340
C ₁₆ H ₁₃ N ₄ Br.	2,6-Dianilino-5-brompyrimidine. <i>Wheeler and Bristol</i>	444
C ₁₆ H ₁₅ O ₃ N.	Dibenzhydroxamic acid ethyl ester. <i>Biddle</i>	62
C ₁₆ H ₁₅ O ₃ N.	β,β -Diphenylmethylmalonic monamide. <i>Kohler and Reimer</i>	342
C ₁₆ H ₁₅ N ₄ Cl.	2,6-Dianilinopyrimidine hydrochloride. <i>Wheeler and Bristol</i>	459
C ₁₆ H ₁₇ ON.	β,γ -Diphenylbutyramide. <i>Kohler and Reimer</i>	355

4 XVI.

C ₁₆ H ₂₄ N ₂ Cl ₈ Hg ₅ .	Mercury haemopyrrol mercuric chloride. <i>Orndorff and Teeple</i>	234
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C₁₇-GROUP.

C ₁₇ H ₃₀ .	Hydrocarbon from petroleum. <i>Mabery</i>	272
C ₁₇ H ₃₄ .	Hydrocarbon from petroleum. <i>Mabery and Palm</i>	257

2 XVII.

C ₁₇ H ₁₂ O.	α -Naphthophenone. <i>Kohler and Reimer</i>	351
C ₁₇ H ₁₄ O.	Dibenzalacetone. <i>Kohler and Heritage</i>	30
C ₁₇ H ₁₆ O ₃ .	Benzhydrol acetoacetate. <i>Bacon</i>	80
C ₁₇ H ₁₈ O.	Diphenylmethyl butenol. <i>Kohler and Heritage</i>	162
C ₁₇ H ₁₈ O ₂ .	Benzhydrol isobutyrate. <i>Bacon</i>	88
C ₁₇ H ₁₈ O ₂ .	1-Dimethyl-2-diphenylpropionic acid. <i>Bacon</i>	89
C ₁₇ H ₁₈ O ₂ .	Diphenylpropionic ester. <i>Kohler and Johnstin</i>	43

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3 XVII.

$C_{17}H_{17}ON$. Cinnamyl ethyl anilide. <i>Kohler and Heritage</i>	31
$C_{17}H_{17}O_2Br$. α -Brom- β,β -diphenylpropionic ester. <i>Kohler and Johnston</i>	40
$C_{17}H_{17}O_3N$. β,γ -Diphenylethylmalonic monamide. <i>Kohler and Reimer</i>	354
$C_{17}H_{38}IAs$. Ethyl triisoamyl arsonium iodide. <i>Dehn</i>	146

C₁₈-GROUP.

$C_{18}H_{32}$. Hydrocarbon from petroleum. <i>Mabery</i>	272
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2 XVIII.

$C_{18}H_{16}O_4$. Phenoquinone. <i>Torrey and Hardenbergh</i>	168
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3 XVIII.

$C_{18}H_{16}O_2N$. Ethyl α,α -bromcyan- β,β -diphenylpropionate. <i>Kohler and Reimer</i>	342
$C_{18}H_{17}O_2N$. Ethyl α -cyan- β,β -diphenylpropionate. <i>Kohler and Reimer</i>	339

5 XVIII.

$C_{18}H_{16}O_6N_2I_4Cu$. Copper diiodotyrosine. <i>Wheeler and Jamieson</i> .	371
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C₁₉-GROUP.

$C_{19}H_{36}$. Hydrocarbon from petroleum. <i>Mabery and Palm</i>	258
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2 XIX.

$C_{19}H_{16}N_2$. Benzophenone phenylhydrazone. <i>Bacon</i>	74
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3 XIX.

$C_{19}H_{13}O_4N$. 5-Nitro-2-oxydiphenyl benzoic ether. <i>Hill and Hale</i>	10
$C_{19}H_{14}O_3S$. <i>o</i> -Benzoyldiphenylsulphone. <i>Weedon and Doughty</i> .	414

C₂₀-GROUP.

$C_{20}H_{18}$. <i>o</i> -Tolyldiphenylmethane. <i>Acree</i>	195
$C_{20}H_{18}$. <i>m</i> -Tolyldiphenylmethane. <i>Acree</i>	195

2 XX.

$C_{20}H_{18}O$.	<i>o</i> -Tolyldiphenylcarbinol. <i>Acree</i>	195
$C_{20}H_{18}O$.	<i>m</i> -Tolyldiphenylcarbinol. <i>Acree</i>	194

3 XX.

$C_{20}H_{17}O_2N$.	Ethyl-1,3-diphenyl-4-cyan-1-pentinate. <i>Kohler and Reimer</i>	356
$C_{20}H_{17}O_3N$.	Naphthylphenylmethylmalonic monamide. <i>Kohler and Reimer</i>	350

5 XX.

$C_{20}H_{22}O_2N_6Cl_6Pt$.	2-Oxy-6-anilinopyrimidine chlorplatinat. <i>Wheeler and Bristol</i>	459
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 C_{21} -GROUP.

$C_{21}H_{40}$.	Hydrocarbon from petroleum. <i>Mabery and Palm</i>	258
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2 XXI.

$C_{21}H_{16}O$.	β -Phenylbenzalacetophenone. <i>Kohler and Johnstin</i> ...	41
$C_{21}H_{16}O_2$.	Triphenylacrylic acid. <i>Kohler and Heritage</i>	159
$C_{21}H_{18}O$.	Diphenylpropiophenone. <i>Kohler and Johnstin</i>	43
$C_{21}H_{18}O$.	Diphenylpropiophenone. <i>Kohler and Heritage</i>	26, 30
$C_{21}H_{18}O_2$.	Triphenylpropionic acid. <i>Kohler and Heritage</i>	156
$C_{21}H_{21}N$.	Tribenzylamine. <i>Clarke</i>	499

3 XXI.

$C_{21}H_{17}OBr$.	Diphenylbrompropiophenone. <i>Kohler and Johnstin</i> 39, 41, 43, 45	
$C_{21}H_{38}IAs$.	Phenyl triisoamyl arsonium iodide. <i>Dehn</i>	152

 C_{22} -GROUP.

$C_{22}H_{42}$.	Hydrocarbon from petroleum. <i>Mabery and Palm</i>	256
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2 XXII.

$C_{22}H_{20}O$.	Tolyldiphenylpropionic acid. <i>Kohler and Heritage</i> ...	160
$C_{22}H_{20}O_2$.	Methyl triphenylpropionate. <i>Kohler and Heritage</i> ...	155
$C_{22}H_{26}O$.	Probably an ether $[C_6H_5CH : C(CH_3)_2]_2O$. <i>Kohler and Heritage</i>	29

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3 XXII.

$C_{22}H_{18}O_2N$. Ethyl α -cyan- β , β -naphthylphenylpropionate. <i>Kohler and Reimer</i>	349
$C_{22}H_{19}O_2Br$. Triphenylbrompropionic ester. <i>Kohler and Heritage</i>	158

4 XXII.

$C_{22}H_{19}O_2BrMg$. Product of the reaction of phenylcinnamic acid with phenylmagnesium bromide. <i>Kohler and Heritage</i>	154
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C_{23} -GROUP.

$C_{23}H_{42}$. Hydrocarbon from petroleum. <i>Mabery and Palm</i>	261
$C_{23}H_{48}$. Tricosane. <i>Mabery</i>	286

2 XXIII.

$C_{23}H_{22}O_2$. Ethyl triphenylpropionate. <i>Kohler and Heritage</i>	156
$C_{23}H_{22}O_2$. Methyl tolyldiphenylpropionate. <i>Kohler and Heritage</i>	159
$C_{23}H_{32}O_{10}$. Ethyl ditrimethylparaconylmalonate. <i>Noyes</i>	363

3 XXIII.

$C_{23}H_{23}ON$. Diphenylpropionethyl anilide. <i>Kohler and Heritage</i> . ..	32
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4 XXIII.

$C_{23}H_{22}ONBr$. Diphenylbrompropionethyl anilide. <i>Kohler and Heritage</i>	33
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C_{24} -GROUP.

$C_{24}H_{44}$. Hydrocarbon from petroleum. <i>Mabery</i>	274
$C_{24}H_{44}$. Hydrocarbon from petroleum. <i>Mabery and Palm</i>	261
$C_{24}H_{46}$. Hydrocarbon from petroleum. <i>Mabery and Palm</i>	260
$C_{24}H_{50}$. Tetracosane. <i>Mabery</i>	287
$C_{24}H_{50}$. Tetracosane. <i>Mabery and Sieplein</i>	280

2 XXIV.

$C_{24}H_{18}O_2$. Dihydroxydiphenyldihydroacenaphthene. <i>Acree</i>	188
$C_{24}H_{22}O_3$. Product of the reaction of acetyl chloride on the addition compound of phenylmagnesium bromide and methyl phenylcinnamate. <i>Kohler and Heritage</i>	158

4 XXIV.

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ERRATA.

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Page.	Line.	
✓620	45	for "Lehner" read "Lenher."
✓620	51	" "Lehner" read "Lenher."
✓630	40	" "Lehner" read "Lenher."

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✓28	13	" "styril" read "styryl."
✓38	19	" "styril" read "styryl."
✓191	5	" "benzsilicate" read "benzilate."
✓183	note 1	" "298, 310" read "298-310."
✓285	30	" "C ₃₄ H ₆₆ " read C ₃₄ H ₇₀ ."
✓336	7	$\begin{array}{c} \text{C}_6\text{H}_5\text{CHC} : \text{C} \begin{array}{l} \nearrow \text{OC}_2\text{H}_5 \\ \searrow \text{OMgBr} \end{array} \\ \quad \\ \text{R} \quad \text{CN} \begin{array}{l} \nearrow \text{OMgBr} \\ \searrow \text{OC}_2\text{H}_5 \end{array} \end{array}$ " "C₆H₅CHC : C $\begin{array}{l} \nearrow \text{OC}_2\text{H}_5 \\ \searrow \text{OMgBr} \end{array}$" read
		$ \begin{array}{c} \text{C}_6\text{H}_5\text{CHC} : \text{C} \begin{array}{l} \nearrow \text{OC}_2\text{H}_5 \\ \searrow \text{OMgBr} \end{array} \\ \\ \text{RCN} \end{array} $
✓341	23	" "C ₁₅ H ₁₅ O" read "C ₁₅ H ₁₅ ON."
✓343	16	" "diphenylcinnamic" read "phenylcinnamic."
✓343	17	" "diphenyl" read "phenyl."
✓343	37	" "diphenyl" read "phenyl."
✓344	4	" "diphenyl" read "phenyl."
✓344	5	" "diphenyl" read "phenyl."
✓356	2	" "Ethyl Cyandiphenylbutyrate" read "Ethyl 1,3-diphenyl-4-cyan-1-pentinate."
✓413	5	" "68.64" read "61.64."
✓498	14	" "C ₉ H ₁₈ N" read "C ₉ H ₁₃ N."
✓520	3	" "übertragen" read "übertragen."
✓526	38	" "esterifys very readily" read "is readily esterified."
✓542	6	" "comes" read "come."

1871

1872

1873

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